1953

The ferromagnetic properties of the rare earth metals

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NOTE TO USERS

THE FERROMAGNETIC PROPERTIES OF THE RARE EARTH METALS

by

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A Dissertation Submitted to the

Graduate Faculty in Partial Fulfillment of

The Requirements for the Degree of

DOCTOR OF PHILOSOPHY

Major Subject: Physics

Approved:

Signature was redacted for privacy.

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Dean of Graduate College

Iowa State College

1953

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I. INTRODUCTION

> . . . from the theoretical standpoint, these substances [the rare earth metals] are much simpler than those of the iron group. Because the 4f electrons are deeply imbedded in the atom, they do not wander appreciably from the atom, and the question of band structure involved in Stoner's "collective electron ferromagnetism" does not enter. For this reason as much experimental information as possible on the rare earth metals is highly desirable.[1]

The recent development of processes at this laboratory for the separation of pure rare earth salts (1) and for the preparation of the pure metals (2) have made it possible to begin experimental researches on the magnetic properties of these elements here. This thesis is a report of the beginning of this experimental research.

The first significant advance in the theory of ferromagnetism[2] was made by Weiss (5) in 1907. Langevin had by this time developed his well known theory of paramagnetism, based on the assumption that the orientation of a molecular dipole of moment μ in a field H is governed by the Boltzmann distribution law. With this hypothesis it can be shown that the moment per unit volume is given by

$$M = N\mu L(\mu H/kT), \qquad (1)$$

where N is the number of molecules per unit volume, and

L(x) is the Langevin function.

$L(x) = \coth x - x^{-1}$.

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[1] Remark by J. H. Van Vleck at Colloque International de Ferromagnetisme et d'Antiferromagnetisme de Grenoble. See (21).

[2] See (3) and (4) for discussions of the theory of ferromagnetism.

The basic assumption made by Weiss was that the effective field acting on the elementary magnet in a ferromagnetic substance was not the applied field H, but rather H + qM, where q is a proportionality constant, independent of temperature and called the Weiss molecular field constant. Substitution of H + qM, in place of H in the Langevin function in equation 1), yields

$$Y = L(\mu[H + qM]/kT), \tag{2}$$

where Y is the ratio of the magnetization to the absolute saturation magnetization, $\frac{M}{M_\mu}$.

This equation provided a theoretical justification for the experimental Curie-Weiss Law above the Curie point, and provided a semi-quantitative explanation for ferromagnetic phenomena below the Curie point.

Debye, using quantum mechanical considerations, replaced the continuous distribution in the Langevin theory by a discrete series of orientations, and developed the well known Langevin-Debye theory of paramagnetism. When a similar extension is made to the Weiss theory, equation 2) becomes

$$Y = B_S \frac{2S\beta(H + qM)}{kT}, \tag{3}$$

where $B_S(y)$ is the Brillouin function

$$B_S(y) = \frac{2S + 1}{2S} \coth\left(\frac{2Sy + y}{2S}\right) - \frac{1}{2S} \coth\left(\frac{y}{2S}\right).$$

Here S is the spin quantum number of the atom and β is the Bohr magneton, $\frac{eh}{4\pi mc}$.

The Debye-Weiss theory was somewhat successful in explaining the reduced magnetization curves of iron, nickel, and cobalt, when the parameter S was chosen as one-half. The discrepancies between the theory and

experiment have long been recognised, particularly in the neighborhood of the Curie point.

In order to bring the theoretical and experimental reduced magnetization curves of iron, nickel, and cobalt into better agreement, and to explain the magnitude of the absolute saturation magnetization of these elements, Stoner's (6, 7) "collective electron theory of ferromagnetism", which is based on the band picture, was developed. However, as observed by Van Vleck, this theory is probably not applicable to the rare earth metals (21).

Bloch (8) has calculated the variation of the saturation magnetization with temperature using a "spin-wave" treatment. For the low temperature approximation (i.e., assuming that only the lowest energy levels are excited), he has shown that the saturation magnetization is linear in $T^{\frac{3}{2}}$. This has been experimentally verified for iron and nickel below 70°K (9). Above 70°K, the experimental values of the saturation magnetization of iron, nickel, and cobalt seem to have a linear T^2 temperature dependence.

The large "molecular field" postulated by Weiss has been explained by Heisenberg (10) as arising from the quantum mechanical forces of exchange acting between electrons of adjacent atoms. It was necessary for Heisenberg to assume that this exchange energy be positive in order to favor the ferromagnetic state. In the high temperature range (i.e., above the Curie point), this theory was also able to provide a theoretical understanding of the empirical Curie-Weiss Law.

The result of the Heisenberg calculation (assuming quenching of the orbital angular momentum) was similar to equation 3) with y replaced by

$$\frac{2SH + 2zJS^2\gamma}{kT} .$$

and the Curie point was given by

$$T_c = \frac{2zJs(s+1)}{kT} .$$

Here, z is the number of nearest neighbors, and J is the exchange integral.

Recently (11) Zener has taken issue with the Heisenberg mechanism of ferromagnetism. He believes that the exchange interaction between the 3d electrons of neighboring atoms in the iron group (presumably the 4f electrons in the rare earths) is such as to oppose ferromagnetism. He proposes that the ferromagnetic state exists only when the positive exchange interaction between the valence electrons of neighboring atoms, which are assumed to be strongly coupled to the 3d electrons, is larger than the Heisenberg-type coupling.

Slater (12) also has recently attacked the usual approximation methods of calculating ferromagnetic phenomena. He has pointed out that these methods, as they are usually applied, are not appropriate for systems containing more than a few electrons. Slater maintains,

> . . . that to treat magnetic problems properly, we must make such calculations (i.e., linear combinations of different determinantal functions, corresponding to different assignments of electrons to orbits) for different total spins, calculate the energy of the states of different magnetizations as a function of internuclear distance, and see which states lie lower, the magnetic or nonmagnetic.

Besides the usual paramagnetic, diamagnetic, and ferromagnetic substances, there is still another class of magnetic materials, those which are antiferromagnetic. These substances show experimentally a monotonically increasing susceptibility with decreasing temperature, which reaches

a maximum at a certain temperature called the Curie temperature.[1] Below the Curie temperature, the susceptibility decreases with decreasing temperature until at absolute zero the susceptibility is 0.3 to 0.85 times its value at the Curie temperature. These substances also show dependence of the susceptibility on field strength, and hysteresis effects below the Curie temperature. The direct experimental test for antiferromagnetism is by neutron diffraction studies.

The behavior of antiferromagnetic substances is explained theoretically in the following way. The crystal is thought to be made up of two or more sublattices A, B, etc., such that the nearest neighbors of atom A are atoms belonging to B and vice versa. In the Heisenberg molecular field, all the spins of neighboring atoms are, on the average, assumed to be parallel. This assumption would be valid if the exchange integral were positive, as then the state with aligned neighboring spins would be the state of lowest energy. However, if the exchange integral is negative, the state of lowest energy is that in which the spins of lattice A are antiparallel to the spins of lattice B. If this type of model is treated by the method analogous to that used for the Heisenberg model an expression is obtained for the Curie temperature, and the Curie-Weiss Law for the paramagnetic behavior above the Curie temperature is again obtained. The decreasing susceptibility with temperature, and the field dependence of susceptibility below the Curie temperature is also understood on the basis of this model. For more detailed descriptions of antiferromagnetism and the mathematical analysis, the reader is referred to the original

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[1] The term "Curie temperature" will be used to designate the temperature below which a substance is antiferromagnetic, as distinguished from the term "Curie point" used to designate the temperature below which a substance is ferromagnetic.

papers of Néel (13, 14), Bitter (15), and Van Vleck (16).

Unfortunately it has been impossible to calculate the sign of the exchange integral for these substances of interest in magnetic phenomena. However, Slater (17) has developed a qualitative rule for predicting the possibility of the existence of the ferromagnetic state for a given substance. It states that the necessary condition for the existence of ferromagnetism is that the atomic radius be small compared to the distance between atoms. Presumably, therefore, when the ratio of R/r (the atomic separation over the radius of the unfilled shell which provides the bulk of the magnetic moment) is small, the exchange integral is negative, and the antiferromagnetic state is favored. As the distance between atoms becomes larger (assuming that r remains constant), the exchange integral becomes positive at a certain critical distance of atomic separation. As R is further increased, the exchange integral also increases in the positive direction until a maximum is reached. A further increase in R decreases the magnitude of the exchange integral. In this region of positive exchange, the ferromagnetic and paramagnetic states are favored.

Briefly this is the present state of magnetic theory. In general, the theories of paramagnetism and diamagnetism (which were not discussed here) have been reasonably successful in both a qualitative and quantitative way. The theories of Weiss, Heisenberg, Stoner, Néel, etc., have yielded a qualitative explanation of ferromagnetism and antiferromagnetism. Perhaps it is due only to the difficulty of the calculations involved in these theories that they are not also completely satisfying from a quantitative standpoint. Nevertheless, by supplying new and more complete

data on the ferromagnetic rare earths, there is hope that a more complete understanding of magnetic phenomena will be obtained.

Three rare earth metals were chosen for this study; gadolinium, dysprosium, and erbium. These metals were selected because they were either known to be ferromagnetic, or there was good reason to believe they were ferromagnetic.

The ferromagnetic properties of metallic gadolinium were reported in 1935 by Urbain, Weiss and Trombe (18), and by Trombe (19). The value of the absolute saturation magnetization was cited as 253.5 cgs units, and the Curie point as 16°C.

Preliminary measurements on gadolinium were made using a ballistic method with the sample in the form of a torus (20). Since there appeared to be certain discrepancies between these preliminary measurements and those reported by Trombe, it was deemed desirable to extend these measurements to higher fields.

Dysprosium has been shown by Trombe (21, 22) to be ferromagnetic. He reported the existence of a magnetic anomaly at 179°K. From 179°K to 105°K he noted that the susceptibility was field dependent. Below 105°K, dysprosium was truly ferromagnetic, having a Curie point at about 105°K. Trombe did not give in his papers a value for the absolute saturation magnetization, or magnetic moment vs. magnetic field isotherms. For this reason, the magnetic measurements on metallic dysprosium were made.

Néel (23), working with the magnetic susceptibility data of Klemm and Bommer (24), predicted a Curie point for erbium at about 40°K. Barson's (20) work on the electrical resistivity of erbium has shown an anomaly at about 70°-80°K. This type of anomaly in the electrical resis-

tivity is closely associated with the magnetic Curie point. Thus, with the hope of finding a new ferromagnetic element, erbium was chosen as the final substance to complete this initial investigation of the magnetic properties of the rare earth metals.

Of all the measurable magnetic quantities of a ferromagnetic substance, only the saturation magnetization, and in particular only the saturation magnetization at absolute zero is alone characteristic of the substance. All other magnetic quantities such as the Curie point, coercive force, remanent magnetization, etc., are dependent to a greater or lesser extent on the past history of the substance. Consequently the primary purpose of this investigation was to determine, if possible, the absolute saturation magnetization of the three elements chosen.

For comparison of experimental data with theory, the variation of spontaneous magnetization, i.e., the magnetic moment of a substance in a zero applied magnetic field, is required. The spontaneous magnetization can be determined from the data obtained in this investigation, but emphasis has not been placed in this direction.

The value of the Curie point is also required to correlate experimental data with theory. In the past it has been the custom to define the Curie point in two different ways. Probably the preferred definition is the temperature at which spontaneous magnetization disappears. The second definition is the temperature at which ferromagnetism disappears in a small, but not vanishing, applied field. Which definition is used seems to depend upon the experimenter and his method of measurement.[1] In

[1]Trombe (18, 19) uses the latter definition for the Curie point determination of gadolinium. He does not state how the Curie point was determined for dysprosium (21, 22). For an example of a Curie point determination using the former definition, see (25).

the measurements of the Curie point of gadolinium reported here, it would appear that these two definitions are not synonymous.

II. EXPERIMENTAL PROCEDURE

A. Materials

The metals used in this investigation were subjected to spectrographic analysis to determine the amount of impurities[1] in parts per million of the following elements: iron, nickel, cobalt, calcium, and other rare earths.

The analysis of the gadolinium metal used was as follows: Ca, detectable but less than 200 ppm; Sm, detectable but less than 600 ppm; Fe, Co, Ni, and other rare earths, not detected.

Dysprosium showed the following impurities: Ca, detectable but less than 100 ppm; Fe, detectable but less than 2000 ppm; Mo, detectable but less than 2000 ppm; Er, detectable but less than 200 ppm; Y, detectable but less than 200 ppm; Ni, Co, and other rare earths not detected.

The erbium analysis showed: Ca, detectable but less than 100 ppm; Y, detectable but less than 100 ppm; Fe, detectable but less than 2000 ppm; Ni, Co, and other rare earths not detected.

Crystal structure studies of gadolinium, dysprosium, and erbium were made at this laboratory concurrently with the magnetic studies (26). The results of this investigation showed the three metals to be hexagonal close packed. The temperature ranges over which the structures were investigated were: gadolinium 130-345°K, dysprosium 47-300°K, and erbium 41-300°K.

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[1]Complete spectrographic standards for determining accurate quantitative amounts of impurities in dysprosium and erbium are not yet available.

B. Method of Measurement

Magnetic moments in this investigation were determined by placing the sample in an inhomogeneous magnetic field and measuring the force exerted on the sample in the direction of increasing field strength. It can be shown (37) that the magnitude of this force is given by:

$$F = m\sigma dH/dx, \tag{4}$$

where F = the force in the x-direction,

m = the mass of the sample,

σ = the magnetic moment per unit mass, and

dH/dx = the magnitude of the gradient of the magnetic field in the x-direction.

For the purpose of discussion, the direction of the magnetic field will be designated as the horizontal or y-direction. The gradient of the field and the force are at right angles to the field and are in the vertical or x-direction.

The magnet used in this study was a 30 kw Weiss-type electromagnet, capable of producing a 20,000 oersted field in a 1½ inch pole gap.

The gradient of the field of the electromagnet was calibrated using a sample of 99.99 per cent pure iron, supplied by Johnson, Mathey and Company, Limited. The iron was assumed to be completely saturated for applied fields greater than 4000 oersteds.[1] The saturation magnetization

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[1] In various sections of this dissertation, values of magnetic moments are cited which were obtained in applied fields of less than 4000 oersteds. No claim is made for the accuracy of the absolute magnitude of these values. It is to be noted, however, that since iron is for all practical purposes saturated (to within 1 per cent) for applied fields greater than 1000 oersteds, the error in the magnet calibration in this range is not large.

at 20°C for this sample was taken to be 217.8 cgs units (28). The calibration was checked using a sample of nickel 99.97 per cent pure and assuming a saturation value of 54.65 cgs units (28). The two separate calibrations agreed to at least 0.8 per cent over the entire range of applied fields.[1]

The inhomogeneous field was produced by a method suggested by Sucksmith (29). The vertical faces of ordinary 60° truncated conical pole pieces were divided into three horizontal sections of equal width (see Figure 1). The upper and lower sections were connected by the middle section which was machined at about 5° from the vertical. A portion of the field was found where the gradient was almost constant over nearly a half-inch; thus, the sample was in a position of stable equilibrium during the weighing process. The magnitude of the gradient produced by this technique varied from 100 oersteds per cm. at low fields, to 1000 oersteds per cm. at high fields.

The use of the Sucksmith-type pole pieces offered three advantages over an inhomogeneous field produced by the fringing field of ordinary 60° truncated conical pole pieces. First, it allowed the full use of the maximum field strength of the magnet, as the sample was placed in the middle of the pole gap (position A, Figure 1) rather than at the edge of the pole gap (position B, Figure 1) where the magnitude of the field has decreased considerably.

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[1]This difference between the two calibrations using different standards is within the standard deviation of the repeatability of a number of calibrations using the same standard. See the section on the discussion of errors.

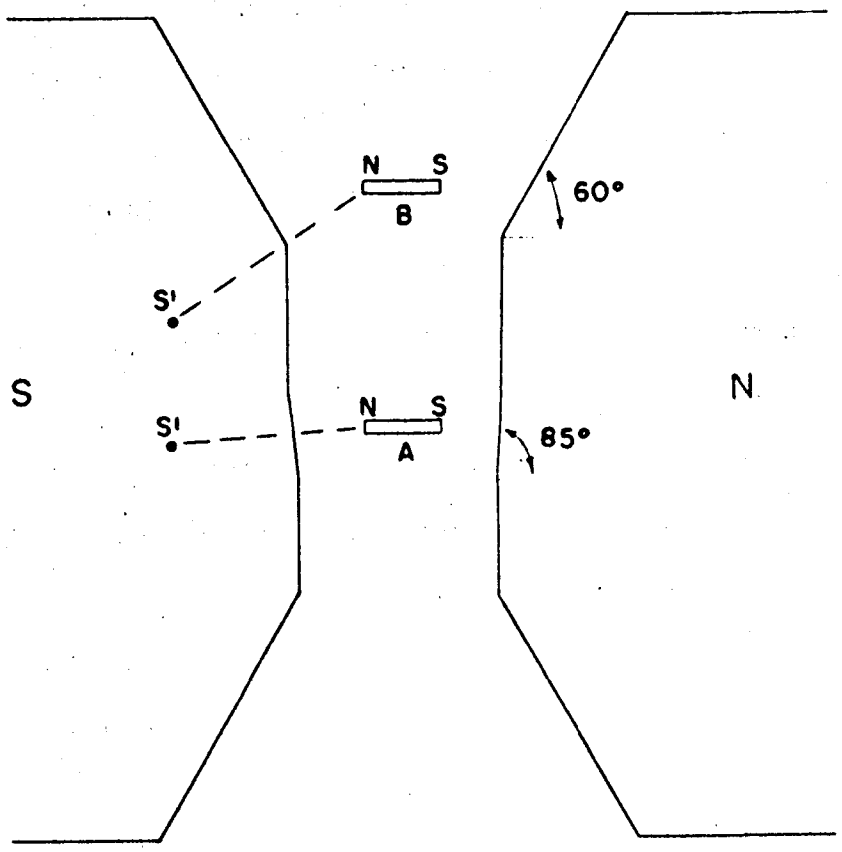

Figure 1. The Sucksmith-type pole pieces used in this study. Sample position A is position used. Position B is sample position used if ordinary truncated conical pole pieces are employed. Points S' are approximate positions of image poles for sample positions A and B, if the permeability of the magnet is assumed infinite.

The second advantage was that the Sucksmith pole pieces provided a larger area over which the gradient of the field was nearly constant. This larger area of constant gradient allowed for faster and more accurate measurements.

The third advantage was that it virtually eliminated the x-component of the force caused by image poles (30). This force is proportional to the permeability of the iron in the magnet and to the square of the total magnetic moment of the sample. In Figure 1 the approximate position for the image pole is designated for the two positions, assuming that the iron in the magnet has an infinite permeability. The use of the Sucksmith-type pole pieces thus reduces any x-component of the image pole force that may be present by approximately a factor of 10 (i.e., $\sin 5°/\sin 60° \approx .1$).

The proportionality factor of the image pole due to the permeability of the magnet is automatically taken into account in the magnet calibration, and does not introduce false measurements in either technique. The proportionality factor due to the total magnetic moment of the sample can not be so easily dismissed. The best one can hope for is that the x-component can be reduced to the point that it can not be detected by the force measuring device used. The Sucksmith-type pole pieces essentially do this. The fact that it was possible to obtain the saturation magnetization of nickel to within 0.8 per cent of the accepted value when the magnetic field was calibrated with iron, showed that the x-component of the image pole force was independent (i.e., not detectable by the measuring apparatus) of the magnitude of the total magnetic moment when the moment

was varied by a factor of four.[1] Since the magnetic moments measured to determine the absolute saturation magnetization in this investigation are comparable to that of iron (within 15 per cent), the image pole force did not limit the accuracy of these measurements.

The magnetic field was measured using a Rawson rotating coil flux-meter.

The calibration samples and the rare earth metal samples were in the form of cylinders, 10 mm long and 1 mm in diameter. The magnetizing field was calculated using the expression

$$H = H_0 - NI, \tag{5}$$

where H = the magnetising field,

H_0 = the applied field,

I = the magnetization per cm^3, and

N = the demagnetising constant, taken to be 0.0875 for samples of the above aspect ratio (31).

Two methods were used for the Curie point determination of gadolinium. In the preliminary measurement, with the torus, the variation of the magnetic moment with temperature was observed for a small constant field. The second method was to observe the variation of the spontaneous magnetization with temperature, using fields produced by the electromagnet. The spontaneous magnetisation was determined by the extrapolation technique of Weiss and Forrer (28).

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[1] In various sections of this dissertation, values of magnetic moments are cited which are less than one-fourth that of iron. The accuracy of the absolute magnitude of these values is therefore not assured.

The Curie points of dysprosium and erbium were determined in a manner to be discussed later.

C. Apparatus

The cryogenic apparatus consisted of a double metal dewar (Figure 2). The sample was placed in the inner dewar, and the temperature of the sample was controlled by a stream of helium gas. The outer dewar contained a heat exchanger and a liquid bath. Helium gas was cooled in the exchanger, then mixed with a stream of warm helium before entering the inner dewar. The temperature range from 26-65°K was obtained with a hydrogen bath, from 85-230°K with nitrogen, 200-280°K with acetone and dry ice, 280-310°K with ice water. The temperature was controlled to within a degree for saturation measurements and to within a quarter of a degree for the Curie point determination, using spontaneous magnetization data.

The temperature was measured by a copper-constantan thermocouple calibrated against a Bureau of Standards calibrated platinum resistance thermometer.

This apparatus was used throughout, except for the 20.4°K data. Here the sample was immersed directly in the liquid hydrogen bath, and the necessary buoyancy corrections made to account for changes in the height of the liquid.

The Curie point determination made with the torus was performed in an alcohol bath and the temperature was controlled to within 0.05°C. A mercury thermometer which gave readings of the true temperature to $\pm$ 0.1°C was used to measure the temperature.

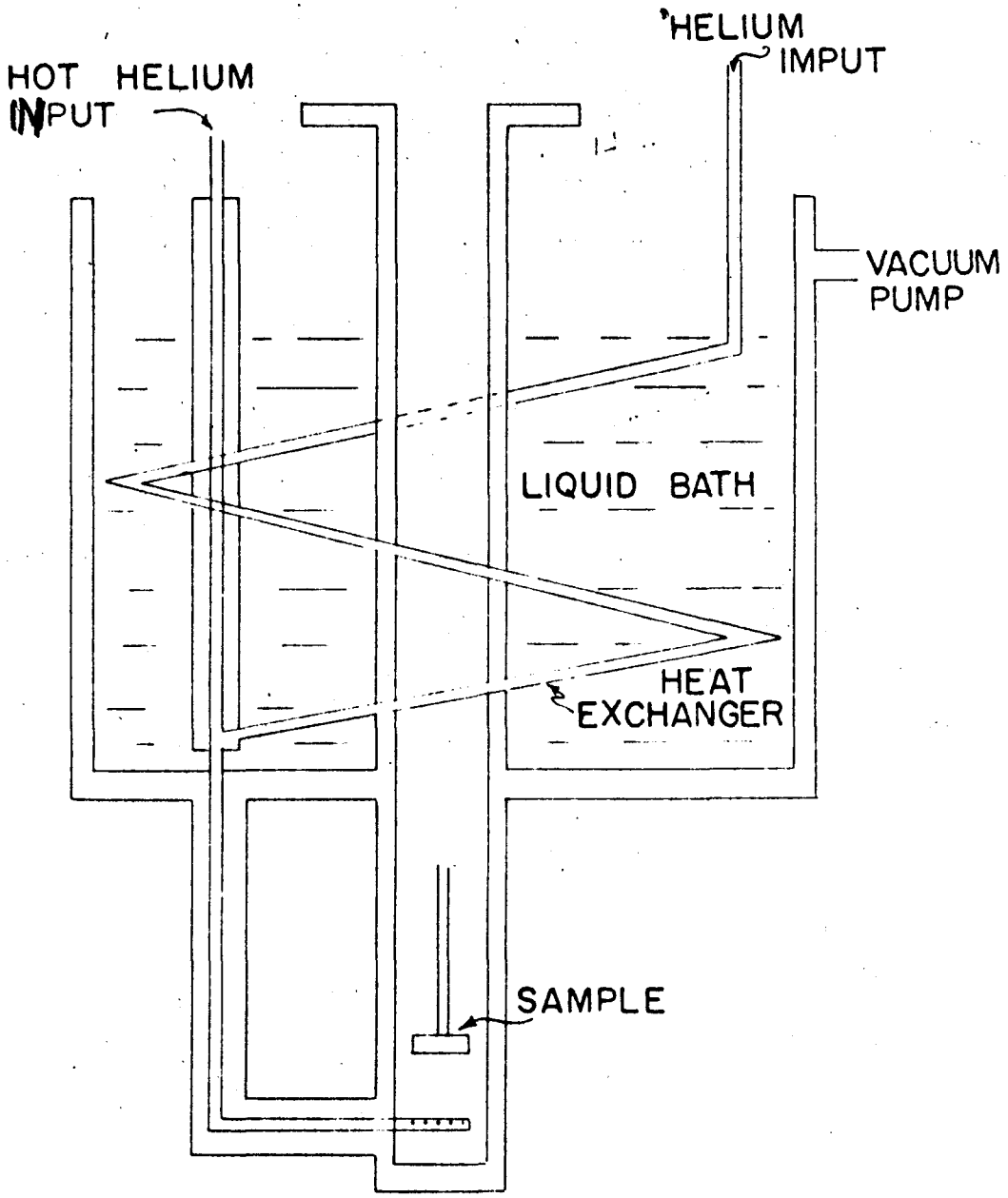


Figure 2. Cryogenic apparatus used to provide temperature control for the sample.

III. RESULTS

A. Gadolinium

Figure 3 shows several of the representative curves of the isothermal variation of the magnetic moment as a function of 1/H for gadolinium. It was found that the variation, for magnetising fields of 4,000-18,000 oersteds over the temperature range of 20-253°K, was well represented by the expression

$$\sigma_{H,T} = \sigma_{\infty,T}(1 - a/H), \tag{6}$$

where $\sigma_{H,T}$ = the magnetic moment per gram,

$\sigma_{\infty,T}$ = the saturation moment per gram at T°K,

H = the magnetising field, and

a = constant.

The data were extrapolated to 1/H equal to zero, using the method of least squares to find the saturation magnetization.

The values of the saturation magnetisation, obtained by the above extrapolation, are plotted as a function of $T^{\frac{3}{2}}$ in Figure 4a. It may be observed that the data seem to agree quite well over the temperature range examined with an expression of the form

$$\sigma_{\infty,T} = \sigma_{\infty,0}(1 - bT^{\frac{3}{2}}) \tag{7}$$

where $\sigma_{\infty,0}$ = the absolute saturation magnetization,

b = a constant, and

T = absolute temperature.

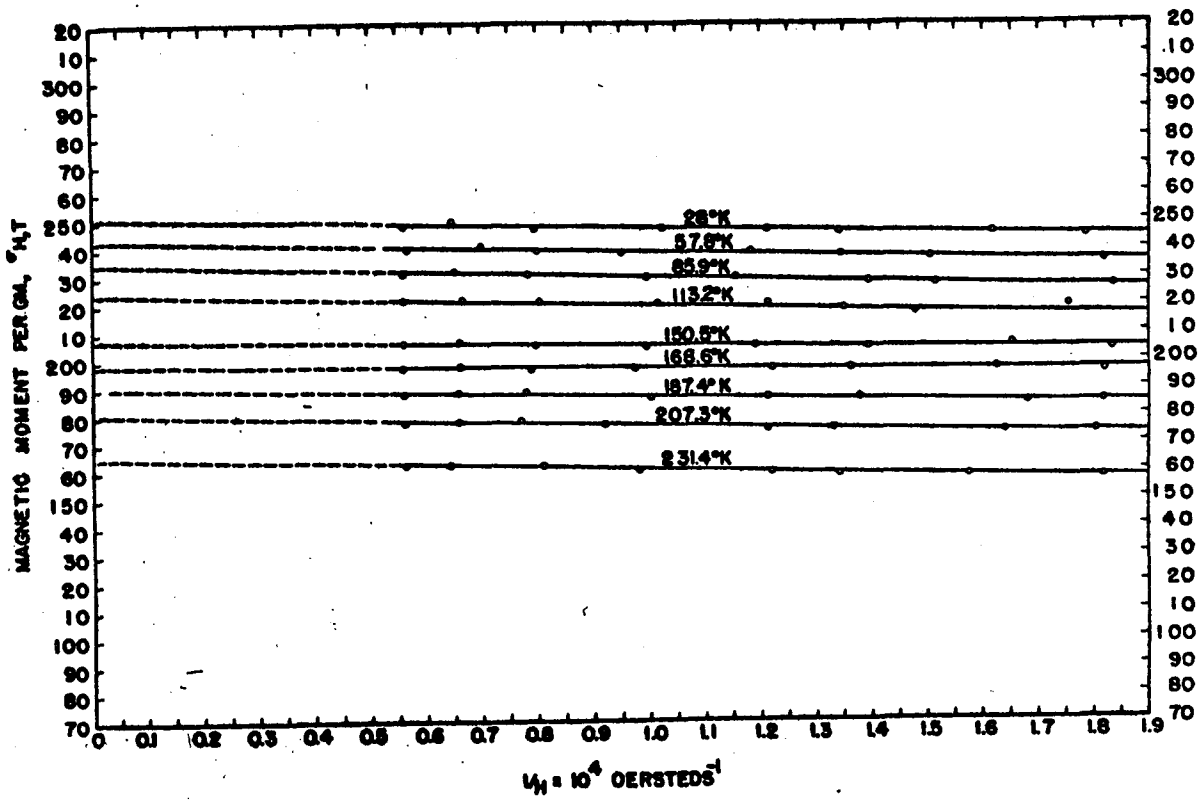


Figure 3. Representative curves of the isothermal variation of the magnetic moment of gadolinium as a function of 1/H.

It may be further observed (Figure 4b) that the data agree fairly well with the expression

$$\sigma_{\infty,T} = \sigma_{\infty,0}(1 - bT^2), \qquad (8)$$

between 250°K and 130°K, but the data seem to fit the $T^{\frac{3}{2}}$ expression at least as well if not better than the T^2 expression over this range. Consequently, the $T^{\frac{3}{2}}$ law was used over the entire range for determining the absolute saturation magnetic moment.

Using again the method of least squares, the value of the saturation magnetization at absolute zero was found to be 253.6 ± 0.9 cgs units. This saturation moment corresponds to 7.18 Bohr magnetons where the value used for the Bohr magneton was 5587 emu per mole (31).

In Figure 5 the ratio of $\sigma_{\infty,T}/\sigma_{\infty,0}$ is plotted as a function of the ratio of T/Θ, where Θ is the Curie temperature. Several curves, obtained from the Debye-Weiss theory of ferromagnetism for various J values, are also shown. To make comparison between experimental data and the Debye-Weiss theory, the ratio of $\sigma_{0,T}/\sigma_{0,0}$, where $\sigma_{0,T}$ is the spontaneous magnetization, should be plotted as a function of T/Θ. However, the value of the spontaneous magnetization differs from the saturation magnetization for gadolinium by only a few per cent, which would not change the location of the plotted points significantly.

The variation of the square of the spontaneous magnetization with temperature near the Curie point is shown in Figure 6b. The intersection of the extension of the nearly linear portion of this curve with the temperature axis was taken to be the Curie point, i.e., 17.7 ± 0.3°C. In Figure 6a the Curie point was determined from data obtained by the ballis-

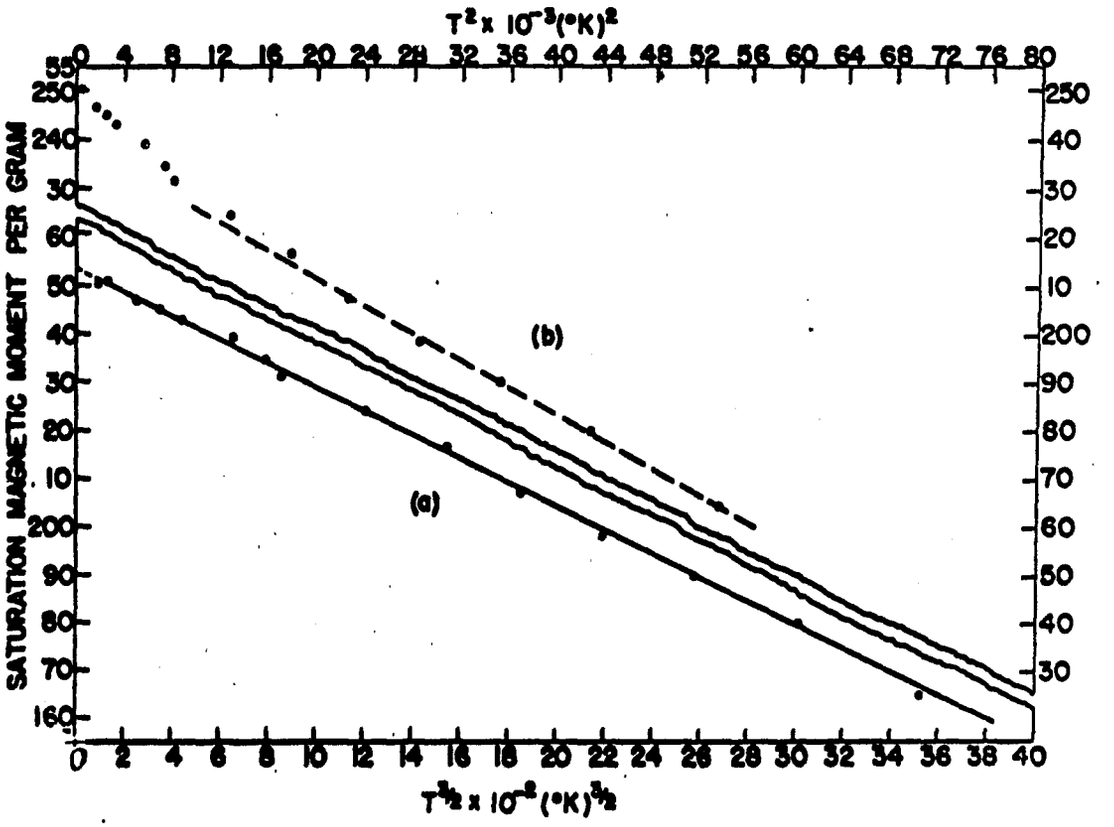


Figure 4 (a) The saturation magnetic moment of gadolinium as a function of $T^{3/2}$ and (b) of T^2.

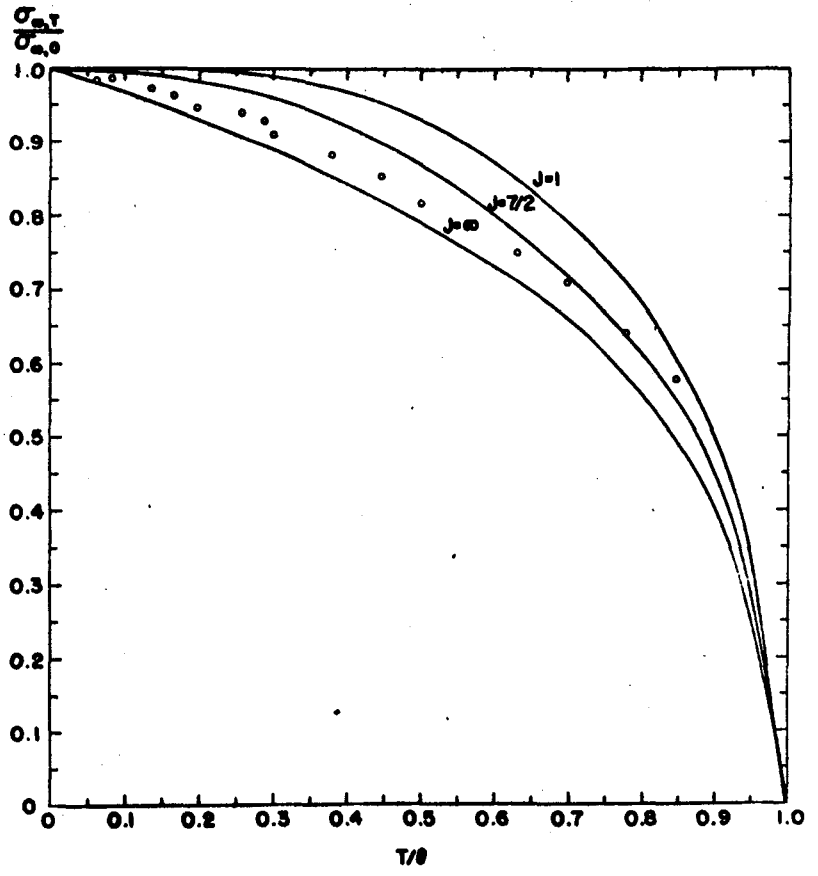


Figure 5. The reduced magnetization curve for gadolinium; also, the theoretical curves for $J = 1$, $J = 7/2$ and $J = \infty$, from the Debye-Weiss quantum theory of ferromagnetism.

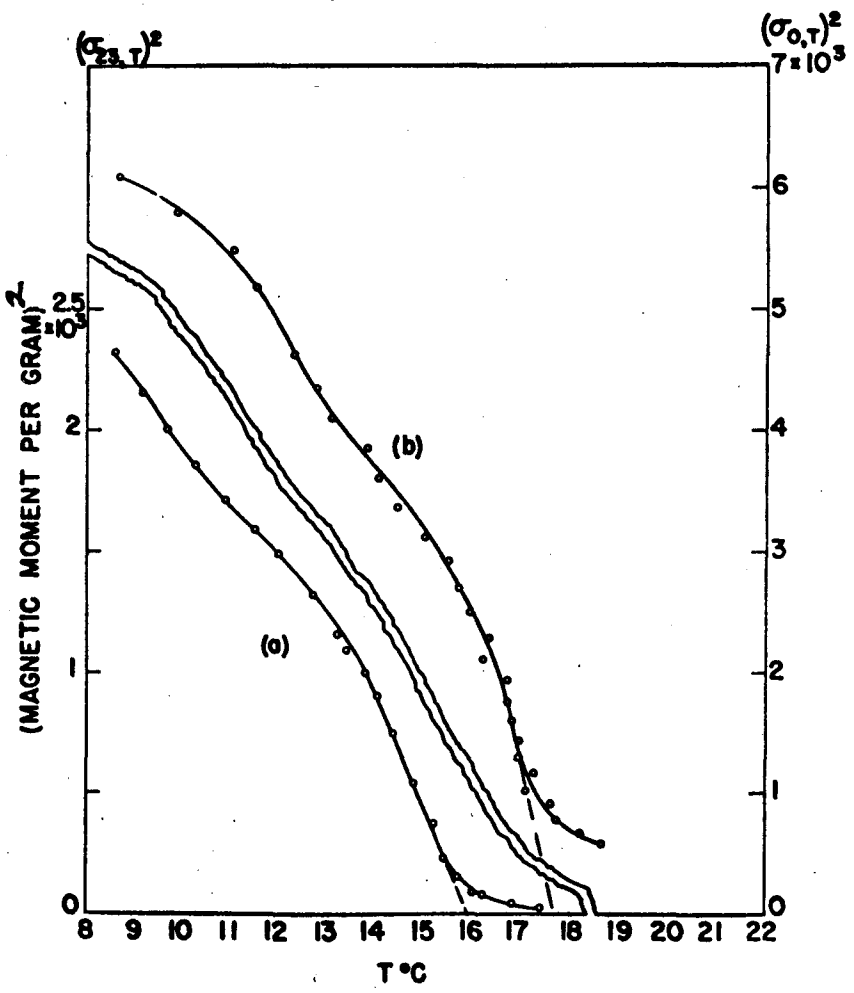


Figure 6 (a) The Curie point determination of gadolinium using the ballistic method and an applied field of 23 oersteds. (b) The Curie point determination using spontaneous magnetization data.

tic method using the torus and a small applied field (i.e., 23 oersteds) and was found to be 15.9 ± 0.1°C.

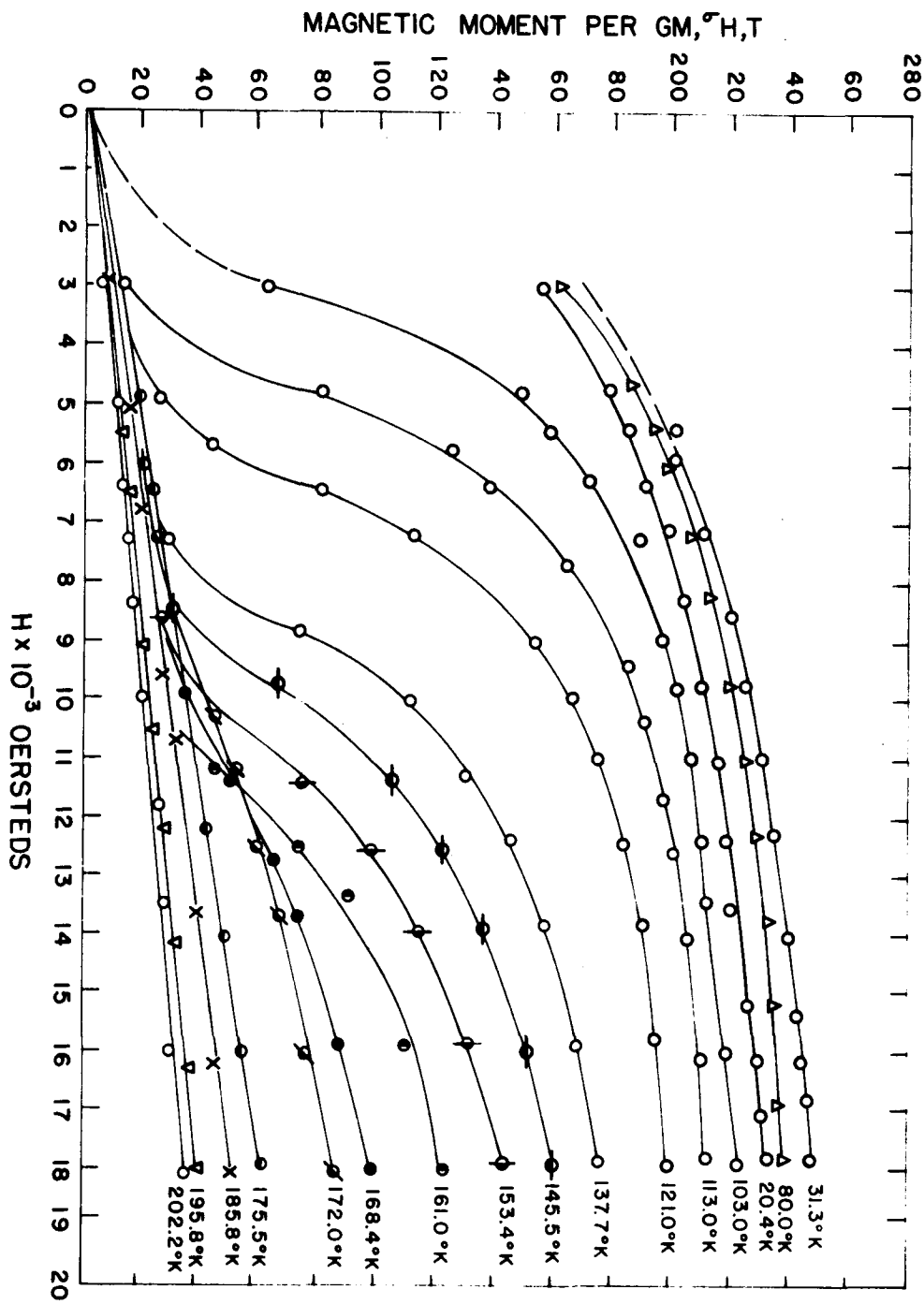
B. Dysprosium

Figure 7 shows a number of the isotherms of the magnetic moment of dysprosium as a function of applied field. Figure 8 is an enlarged portion of the low field region of Figure 7. The initial susceptibility (i.e., the susceptibility calculated from the low field, linear portion of the curves in Figure 7) from 113°-202°K plotted as a function of temperature is shown in Figure 9. One notes that for applied fields up to 18,000 oersteds the σ vs. H isotherms remain linear down to about 175°K. Below 175°K, the isotherms are linear in the low field region, but at some higher field the susceptibility becomes field dependent. As the temperature is lowered below 175°K, the field for which the susceptibility becomes field dependent is smaller.

Below 110°K the magnetisation curves for dysprosium are much the same as those for gadolinium, and are typical of a ferromagnetic substance. It is observed that the element is very magnetically "hard" in comparison to iron or even gadolinium, and is far from saturation in a field of 18,000 oersteds. One also notes that below 103°K, dysprosium becomes rapidly temperature saturated, i.e., temperature has little effect upon the magnitude of the magnetisation.

The 20.4°K data deserve special notice. The curve falls far below the 31.25°K isotherm. These data were taken by a different method from the other isotherms as pointed out above. It has not been possible to

Figure 7. The magnetic moment of dysprosium as a function of applied field for several temperatures.


MAGNETIC MOMENT PER GM, σH,T
H x 10⁻³ OERSTEDS
31.3° K
80.0°K
20.4°K
103.0°K
113.0°K
121.0°K
137.7°K
145.5°K
153.4°K
161.0 °K
168.4°K
172.0°K
175.5°K
185.8°K
195.8°K
202.2°K

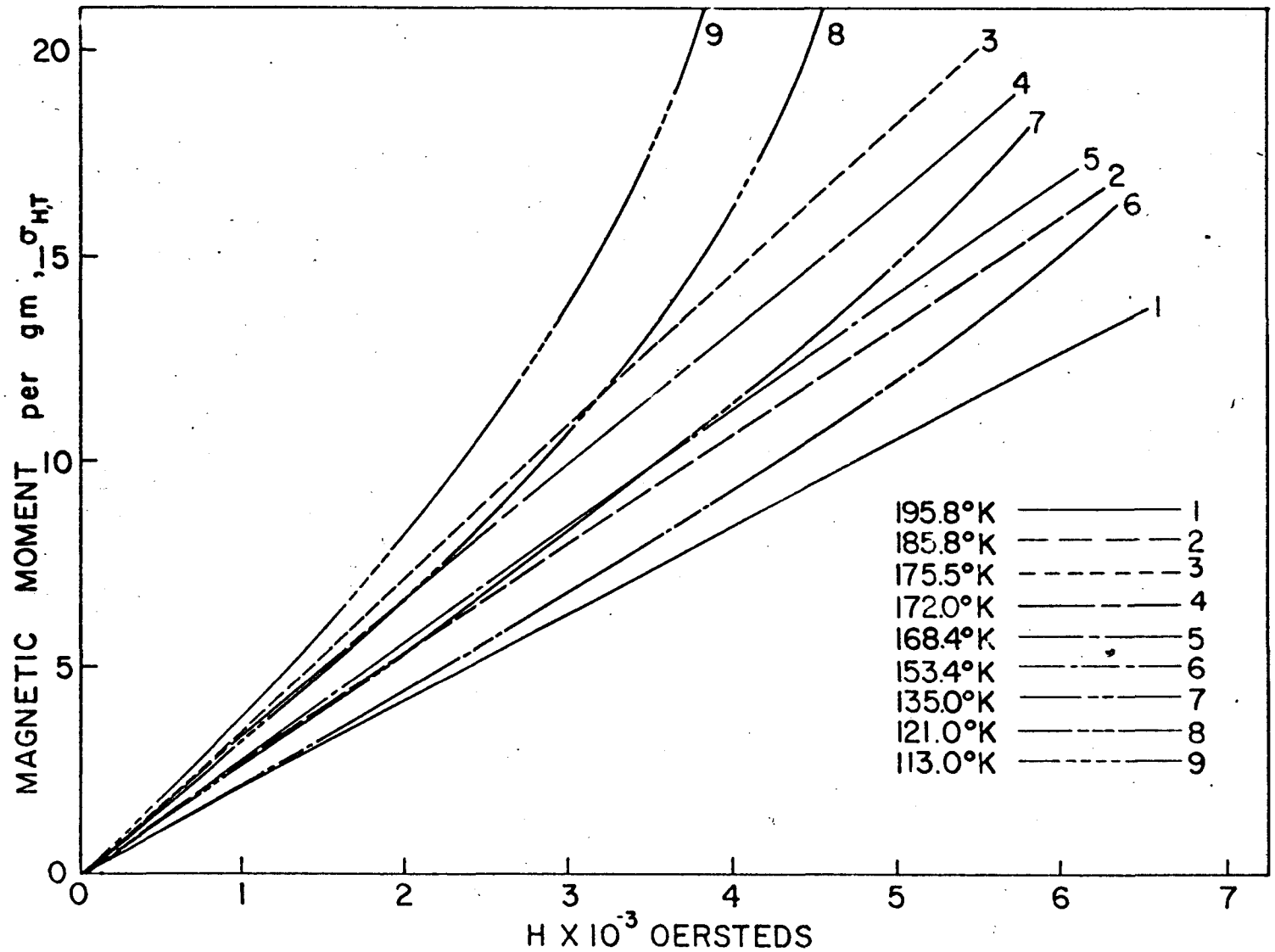


Figure 8. An enlarged plot of the low field region of Figure 7, showing the anomaly in dysprosium observed by Trombe.

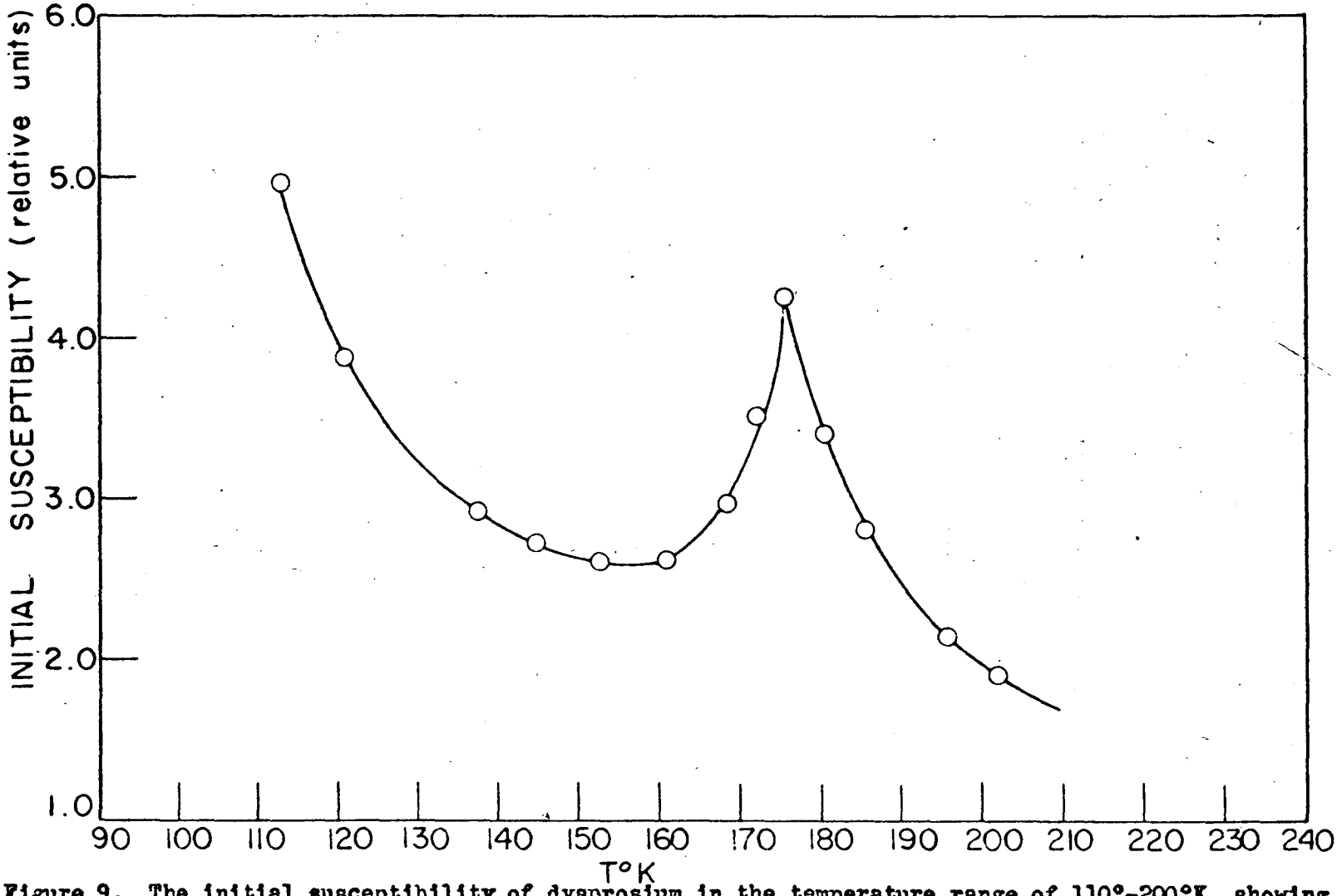


Figure 9. The initial susceptibility of dysprosium in the temperature range of 110°-200°K, showing the anomaly observed by Trombe.

overlap the temperature ranges of the two methods, hence it is not possible to state unequivocally that the anomaly is real; one might attribute the result to a fault in one of the methods of measurement. It is to be noted, however, that no such inconsistency was evident in the data for gadolinium at 20.4°K.

The anomaly observed by Trombe is quite evident in Figure 7 and in Figures 8 and 9. The general shape of the curve in Figure 9 above 165°K is not unlike the corresponding curve for an antiferromagnetic substance in the neighborhood of its Curie temperature.

In order to discuss the magnetic behavior of dysprosium, three or possibly four temperature regions or magnetic states may be distinguished. The first state, P, occurs above 176°K where the element appears to be truly paramagnetic. The second state (hereafter called state A_1) occurs in the temperature range bounded by the anomaly at 176°K and by the ferromagnetic Curie point at about 92°K. (The Curie point determination is discussed below.) The magnetic behavior of dysprosium in this temperature range is characterized by the field dependence of the susceptibility, and the apparent lack of spontaneous magnetization. It is to be noted that this type of behavior is somewhat similar to the behavior of an antiferromagnetic substance below its Curie temperature.

The third magnetic state of dysprosium (hereafter called state F), occurs below about 92°K. Here the element appears to be in a true ferromagnetic state, characterized by spontaneous magnetization, saturation effects, and by hysteresis effects.

A fourth magnetic state may exist for dysprosium (hereafter called state A_2) in the temperature range below about 25°K as indicated by the

anomalous behavior of the 90.4°K isotherm.

The difficulty encountered in attempting to obtain the Curie point of state P from spontaneous magnetization data may also be seen from the magnetization curves (Figure 7). In order to determine the Curie point by this method, it is necessary to obtain spontaneous magnetization data as a function of temperature from the magnetization curves above and below the Curie point. Because of the strange behavior of dysprosium immediately above its Curie point (i.e., in state A_1), it was found impossible to obtain spontaneous magnetization data which were complete enough to allow an accurate determination of the Curie point by this method.

In Figure 10 the Curie point is determined by extrapolation of the linear portion of the σ°_{1200} vs. T curve to the temperature axis. The σ_{1200} data were obtained in a relatively weak field of 1200 oersteds. The value of the Curie point determined by this method is 92°K. Because the Curie point is somewhat dependent on the value of the applied field used in its determination, 92°K is probably several degrees higher than the value of the Curie point determined in a nearly zero applied field.

Figures 11, 12, 13 and 14 are plots of the magnetic moment vs 1/H for several of the isotherms of Figure 7. These curves differ considerably from the corresponding curves of gadolinium. The curves in the neighborhood of 100°K are nearly linear above 5,000 oersteds. At temperatures above 100°K, the curves are concave downward. The curves below 80°K seem to consist of two nearly straight intersecting lines.

Both of the linear sections of these curves have been extrapolated to infinite fields to obtain the saturation moments. No attempt was made to use the method of least squares in these extrapolations.

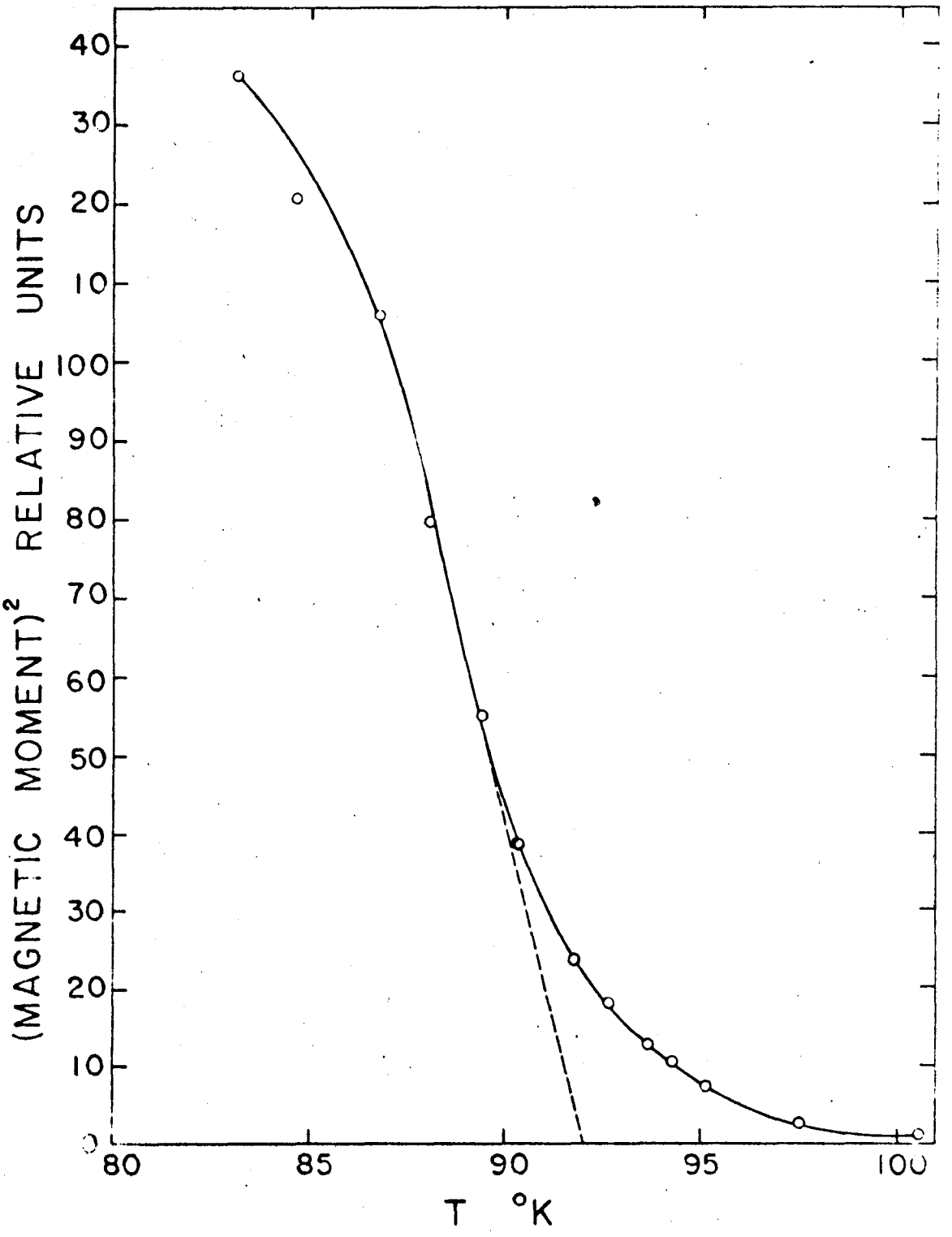


Figure 10. The Curie point determination for dysprosium state F using an applied field of about 1200 oersteds.

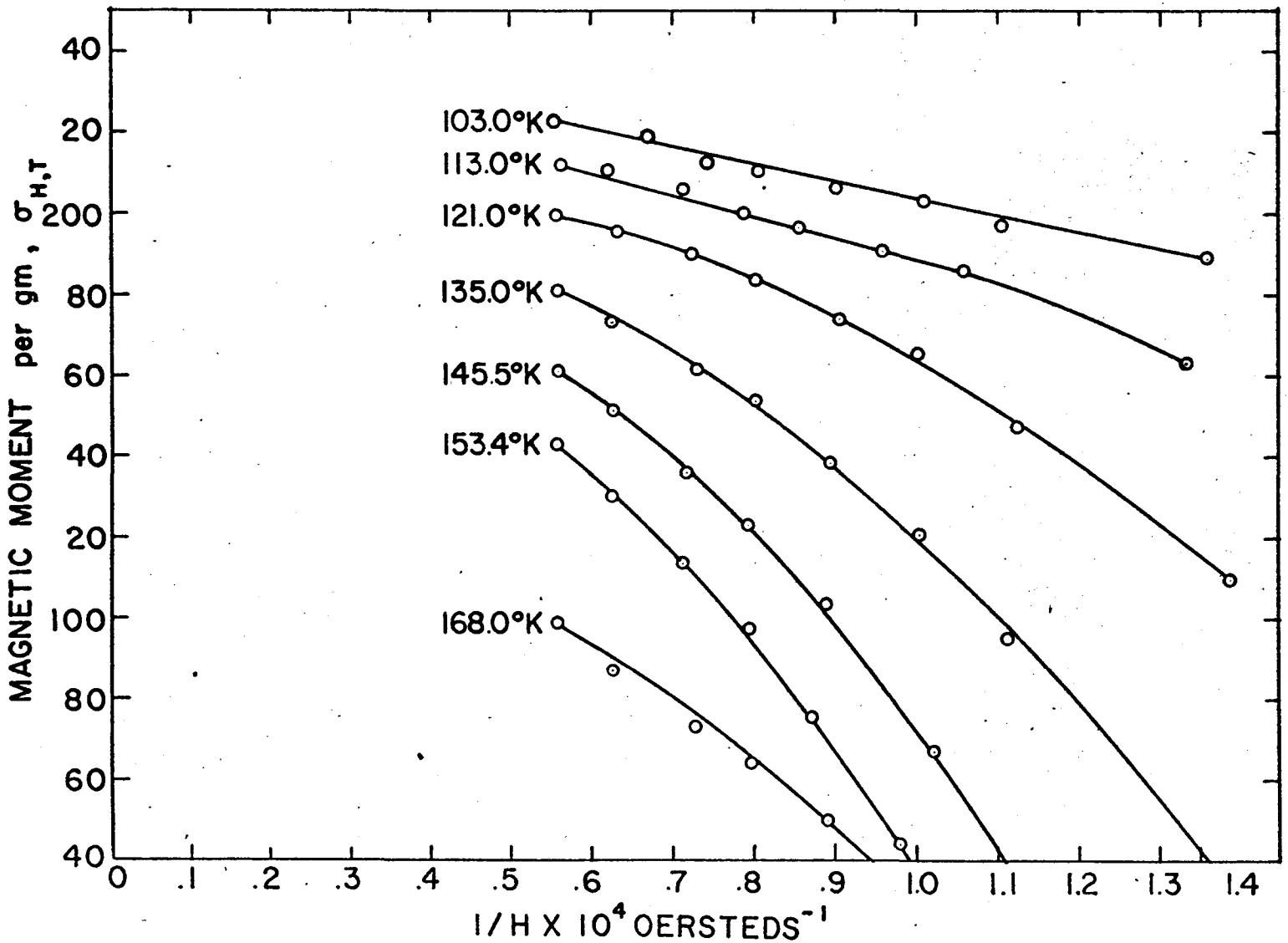


Figure 11. Representative curves of the isothermal variation of the magnetic moment of dysprosium as a function of 1/H.

Figure 12. Representative curve of the isothermal variation of the magnetic moment of dysprosium as a function of 1/H.

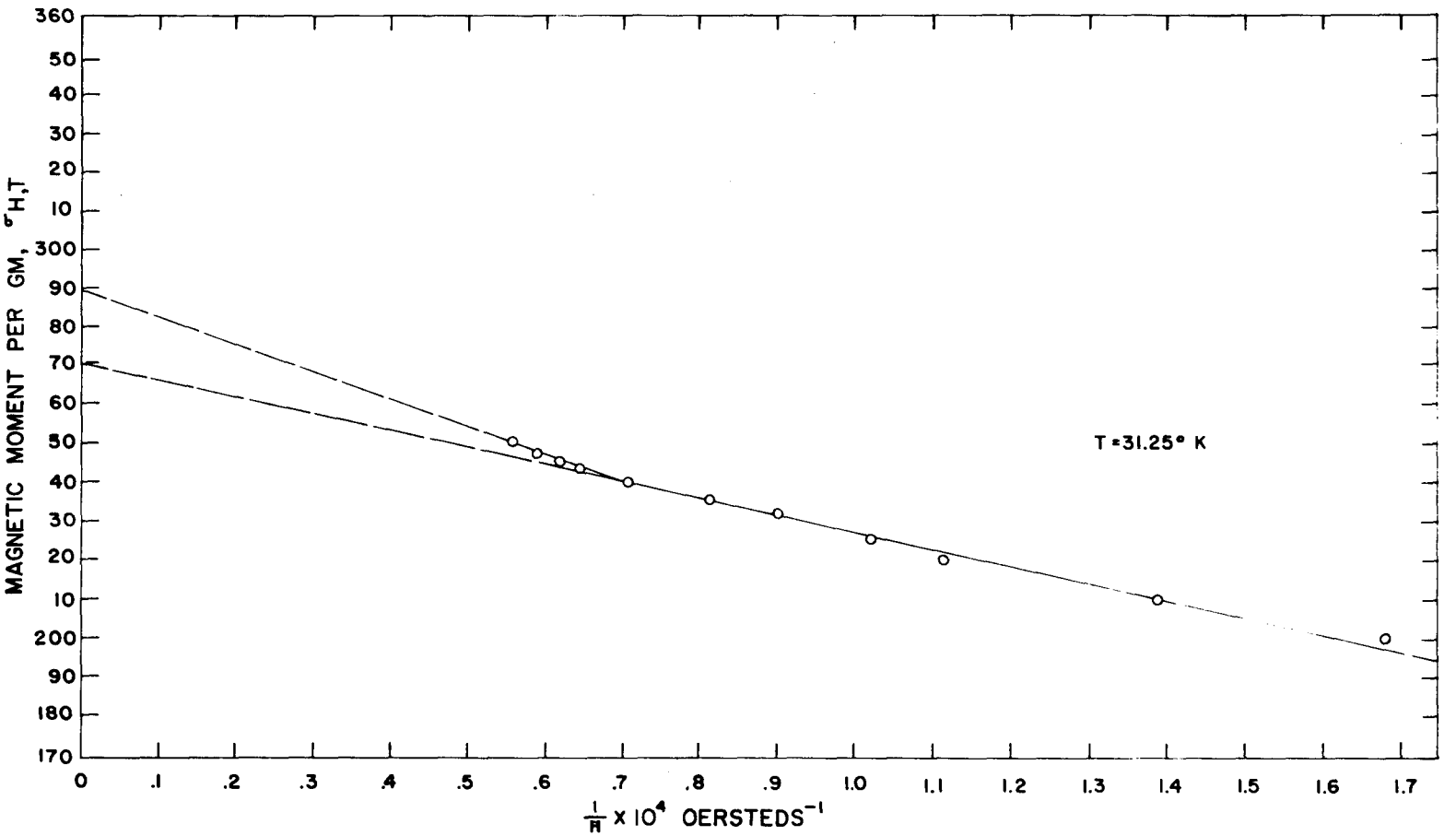

MAGNETIC MOMENT PER GM, $\sigma_{H,T}$
360
50
40
30
20
10
300
90
80
70
60
50
40
30
20
10
200
90
180
170
T = 31.25° K
0
.1
.2
.3
.4
.5
.6
.7
.8
.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
$\frac{1}{H} \times 10^4$ OERSTEDS^{-1}

Figure 13. Representative curves of the isothermal variation of the magnetic moment of dysprosium as a function of 1/H.

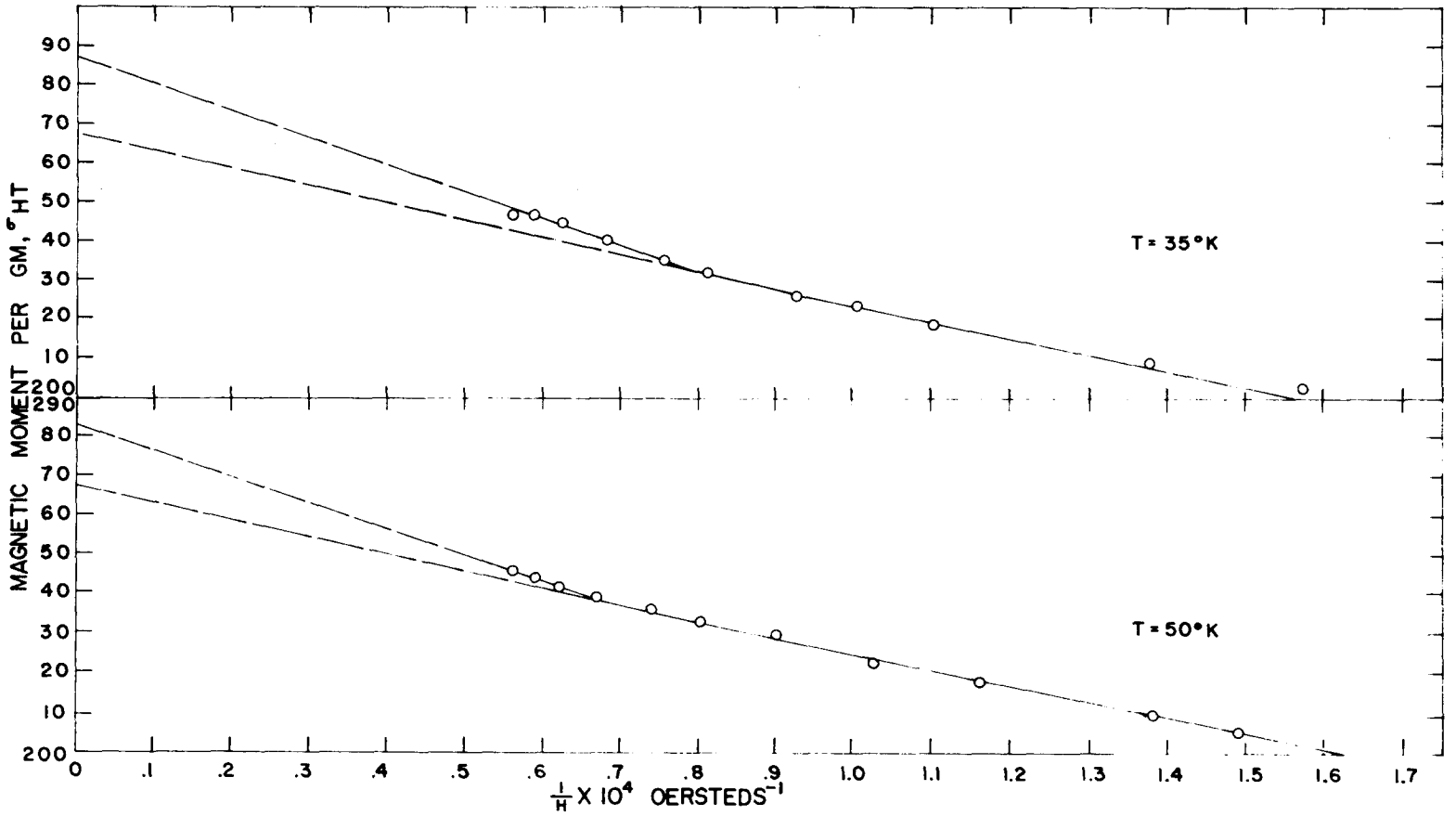
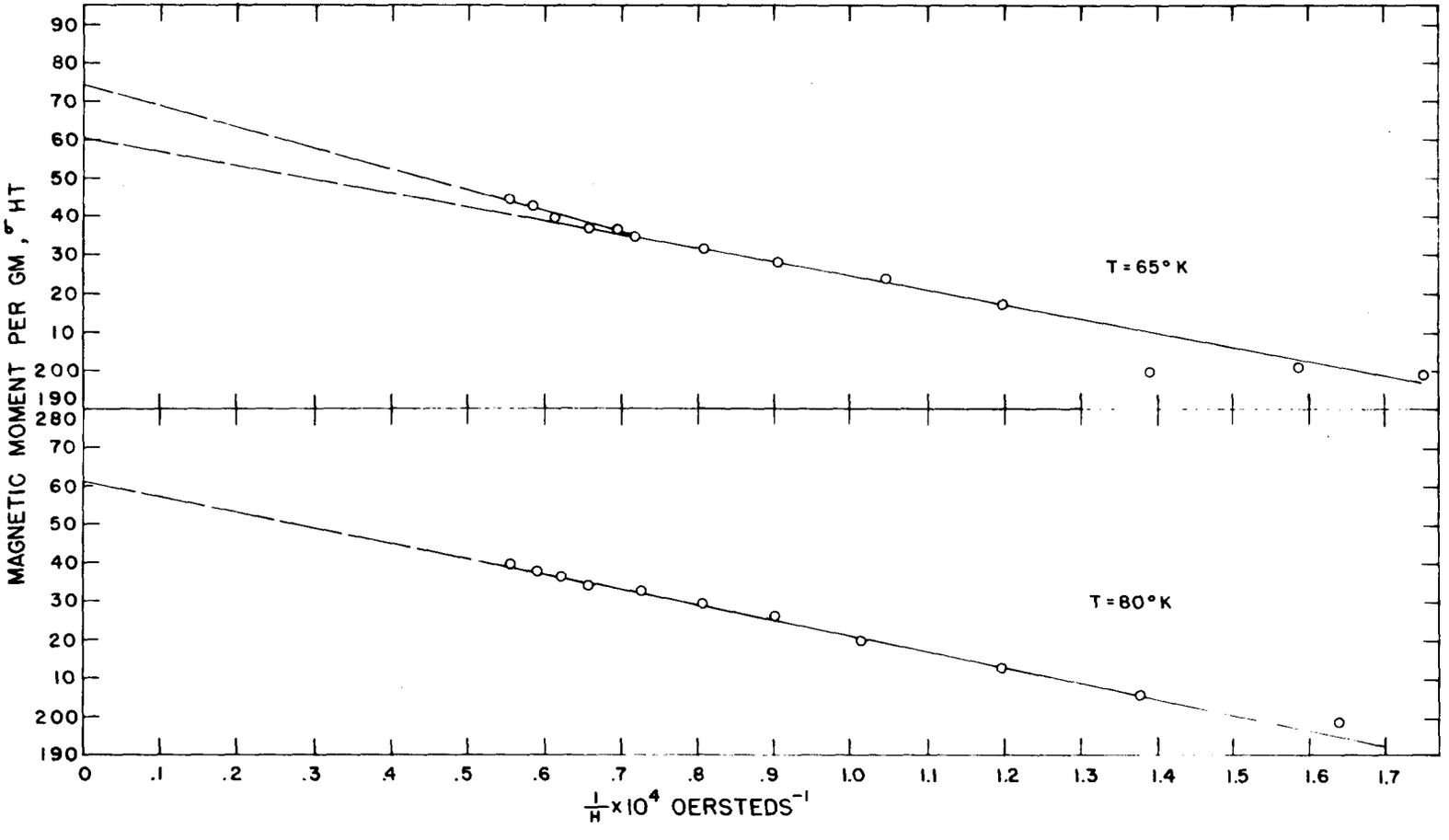

MAGNETIC MOMENT PER GM, σ HT
90
80
70
60
50
40
30
20
10
200
290
80
70
60
50
40
30
20
10
200
T = 35°K
T = 50°K
0
.1
.2
.3
.4
.5
.6
.7
.8
.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1/H X 10⁴ OERSTEDS⁻¹

Figure 14. Representative curves of the isothermal variation of the magnetic moment of dysprosium as a function of 1/H.


MAGNETIC MOMENT PER GM, σ HT
90
80
70
60
50
40
30
20
10
200
190
280
70
60
50
40
30
20
10
200
190
T = 65° K
T = 80° K
0
.1
.2
.3
.4
.5
.6
.7
.8
.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1/H x 10^4 OERSTEDS^-1

In Figure 15 the saturation moments obtained from Figures 12, 13, and 14 are plotted as a function of $T^{\frac{3}{2}}$ (the 20.4°K data have not been considered) to obtain the absolute saturation moment. The saturation moment at absolute zero for dysprosium appears to be about 299 ± 5 cgs units if one uses saturation moments from the high field extrapolations, and about 273 ± 3 cgs units, if one uses the low field extrapolated saturation moments. These moments correspond to 8.7 Bohr magnetons, and 8.0 Bohr magnetons respectively.

It is to be noted that these absolute saturation moments were obtained using data from the temperature range of 31°-80°K only, and therefore only attempt to point out what the approximate magnitude of the saturation moment at absolute zero would be assuming that no further anomalies occur between 0°-31°K.

C. Erbium

Figure 16 shows several of the magnetic isotherms for erbium. Above about 55°K erbium is paramagnetic as indicated by the linear magnetic isotherms at 71.0°K and 61.3°K. Below 51°K (state A_1) its susceptibility becomes field dependent, but there is no evidence of spontaneous magnetization. At the hydrogen point erbium seems to be in a true ferromagnetic state (state F). The extreme magnetic "hardness" of this state is to be noted.

The similarity of the magnetic behavior of erbium and dysprosium is quite evident. However, the anomaly associated with state A_1 of dysprosium is not apparent in the corresponding state of erbium (see Figure 17, where

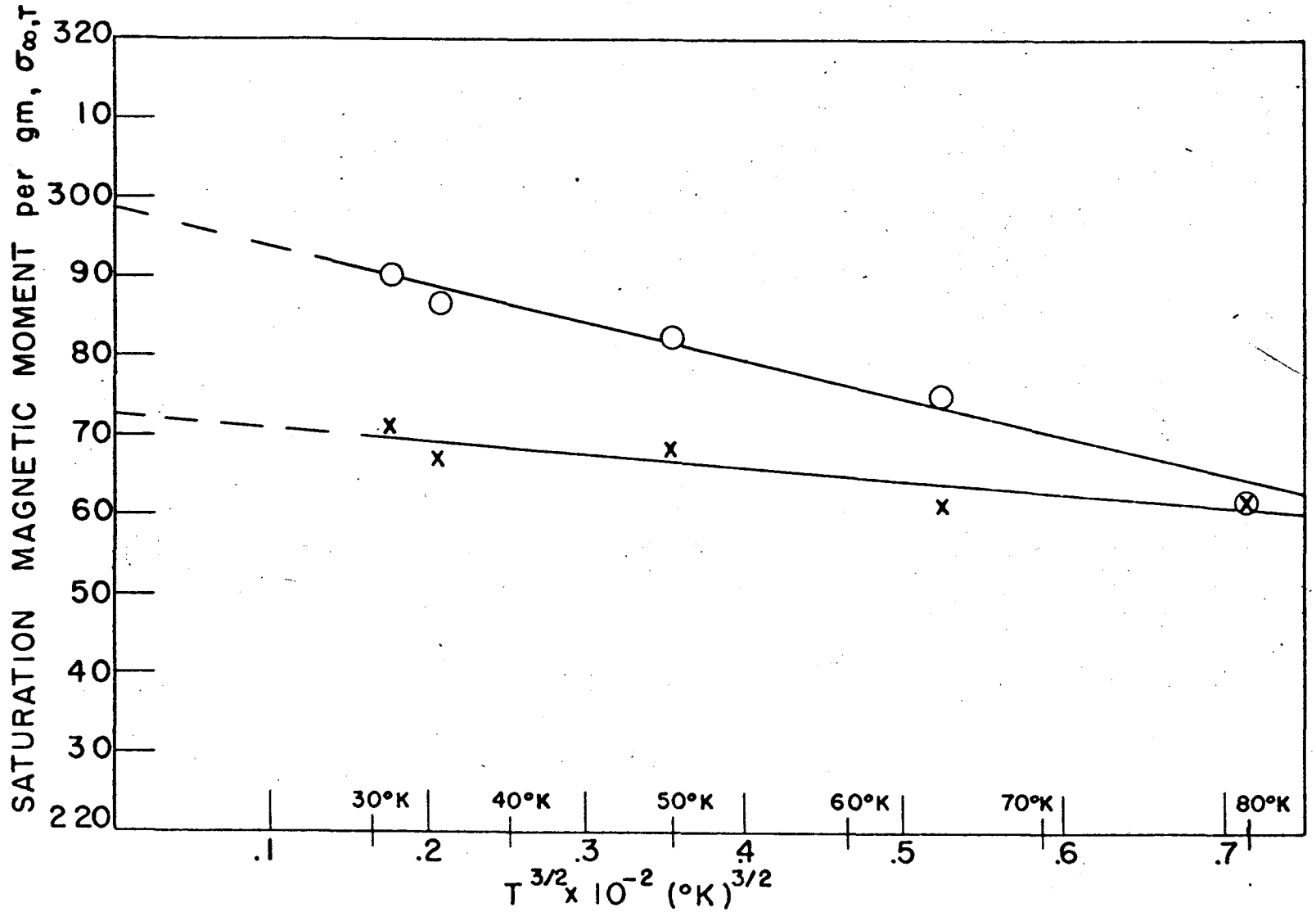
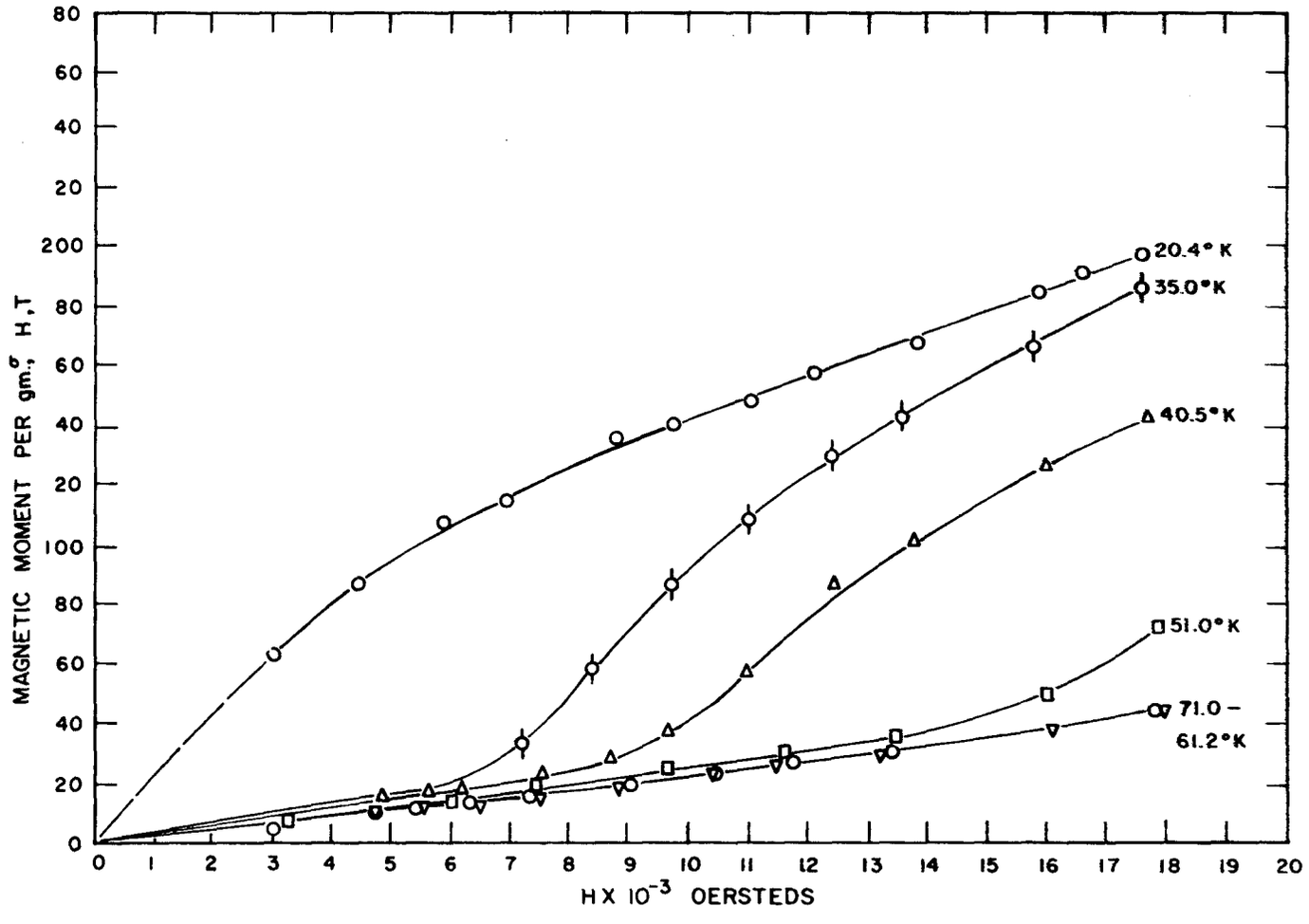


Figure 15. The saturation magnetic moment of dysprosium as a function of $T^{3/2}$. The open circles are saturation magnetization values obtained from the high field extrapolations. The crosses are saturation magnetization values obtained from the low field extrapolations.

should be $T^{3/2} \times 10^{-3}$

Figure 16. The magnetic moment of erbium as a function of applied field for several temperatures.


MAGNETIC MOMENT PER gm., σ H,T
HX 10^-3 OERSTEDS
20.4° K
35.0°K
40.5°K
51.0°K
71.0 –
61.2°K

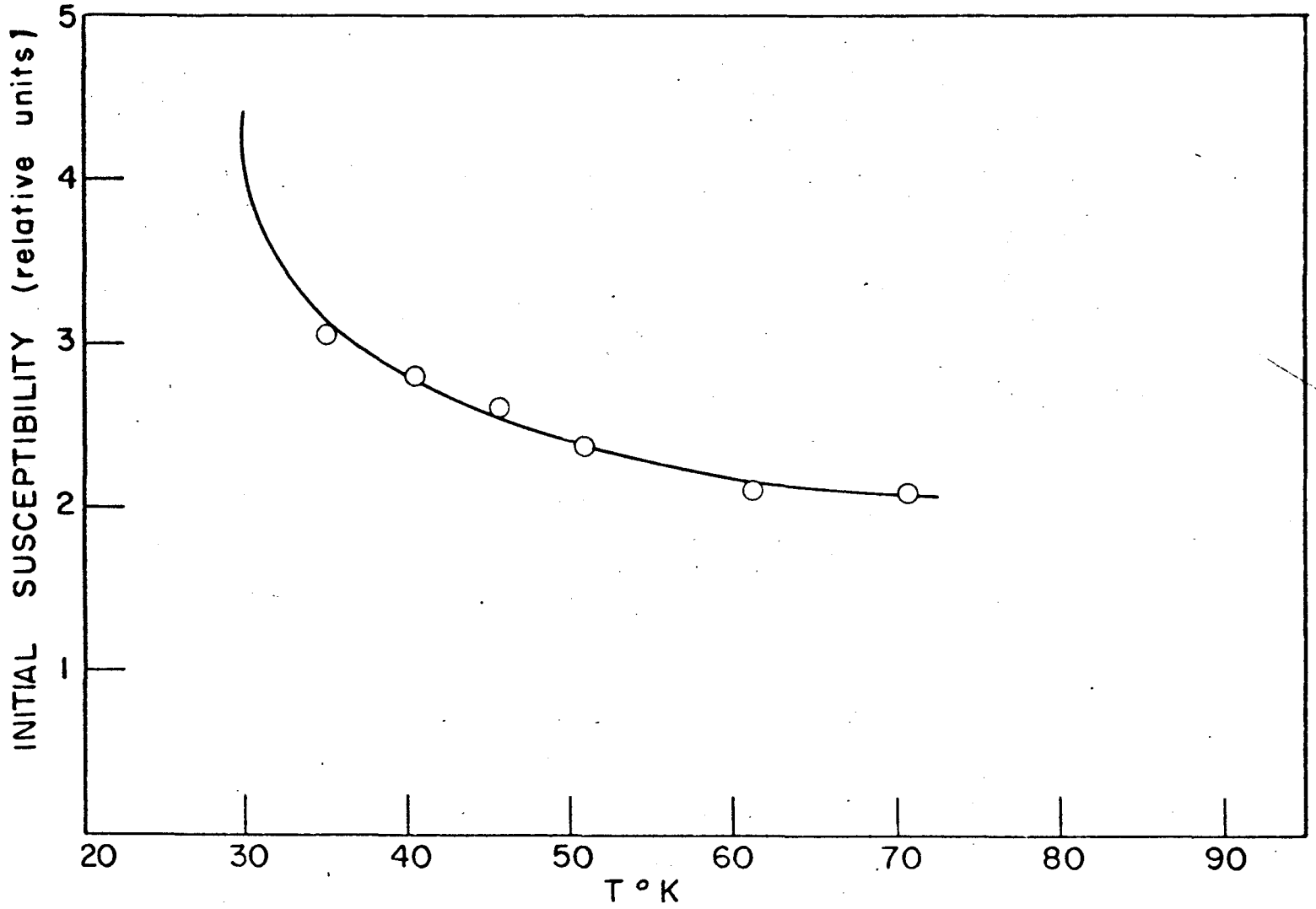


Figure 17. The initial susceptibility of erbium in the temperature range of 35°-71°K.

the initial susceptibility of erbium is plotted as a function of temperature). It may be that the measuring apparatus was not sensitive enough to allow the observation of the anomaly, or that the wrong temperatures were chosen; but, in any case, it is apparent that the anomaly is not as well developed in erbium as in dysprosium, if it exists at all.

The temperature at which the susceptibility of erbium becomes field dependent may be cited as 56.0 ± 5°K.

The σ vs. $1/H$ curve for the 20.4°K data of erbium is quite similar to those of dysprosium. That is, the curve seems to consist of two intersecting straight lines. Extrapolation of the high field region of this curve to $1/H = 0$ indicates that the saturation magnetization of erbium at 20.4°K is of the order of 285 cgs units, corresponding to about 8.6 Bohr magnetons per atom.

Because of the incompleteness of the data, no attempt has been made to determine experimentally the ferromagnetic Curie point of state F, nor was it possible to determine the absolute saturation moment of erbium.

Assuming a "Law of Corresponding Status" to be valid for erbium and dysprosium, the ferromagnetic Curie point of erbium may be estimated. Using the temperature at which the susceptibilities of dysprosium and erbium become field dependent (i.e., 176°K and 56°K respectively), together with the ferromagnetic Curie point of dysprosium (i.e., 92°K), the Curie point of erbium would be about 29°K.

IV. DISCUSSION OF RESULTS

A. Gadolinium

Of particular interest is the fact that the value of the absolute saturation magnetization obtained by Trombe by extrapolation of a T^2 plot agrees exceedingly well with the value obtained here using an extrapolation of a $T^{\frac{3}{2}}$ plot. Of interest also is the fact that the saturation magnetization of gadolinium is linear in $T^{\frac{3}{2}}$ over nearly its entire ferromagnetic range. Gadolinium thus seems to be peculiar in this respect as ferromagnetics, other than the rare earths, are linear in $T^{\frac{3}{2}}$ only at very low temperatures.

This investigation also showed that gadolinium is not as magnetically "hard" as indicated by Trombe, although considerably "harder" than iron. The constant (a) in equation 6) is an indication of this "hardness" and has the value of about 170 oersteds from the data reported here. This is to be compared with Trombe's value of 1250 oersteds (for iron, $a \approx 10$ oersteds). This difference of "hardness" between samples studied here and Trombe's was also indicated by the preliminary measurements at low fields (20), using the ballistic method.

The Curie point found by the ballistic method, Figure 6a, agrees quite well with Trombe's value, where he has defined the Curie point as the temperature at which ferromagnetism disappears in a small field. The Curie point is found to be some two degrees higher when it is defined as the temperature at which spontaneous magnetization disappears. The

disagreement between the values of the Curie points does not seem unreasonable when the differences in their definitions are considered.

It was possible to repeat the data obtained by the ballistic method irrespective of whether the Curie point was approached from above or below, showing there was no temperature hysteresis (within at least 0.1°) at the Curie point.

It should also be mentioned that there was found to be no shift in the Curie point due to annealing. Such a shift was indicated by Curie point determination by electrical resistivity measurements on gadolinium at this laboratory (33). However, there is no definite assurance that the samples used for magnetic measurements were not previously annealed in the casting process.

It may be observed that the absolute saturation magnetization is some 2 per cent higher than would be predicted if only the spins of the 4f electrons contributed to the magnetization; this deviation is believed to be outside the experimental error. Also, the reduced magnetization data points fall far below the curve calculated for the $^8S_{7/2}$ spectrographic state using the Debye-Weiss theory of ferromagnetism. Had $\sigma_{0,T}$ data been used for this plot rather than $\sigma_{\infty,T}$ data, the experimental points would have been slightly lower than the points shown.

B. Dysprosium

The experimental results of the magnetic properties of dysprosium are probably the most interesting of the three elements studied. Although the magnetic behavior is very complicated, and is far from being understood

theoretically, it is felt that the above experimental data will eventually have a significant effect on the theory of ferromagnetism.

The high magnetic moment of dysprosium is of considerable theoretical significance. Magnetic moments have been measured of the order of 245 cgs units for dysprosium. Such a magnetic moment corresponds to about 7 Bohr magnetons. The spectroscopic state of the dysprosium ion is a $^6H_{15/2}$, and, from the paramagnetic theory of Hund and Van Vleck (4), (where it is assumed that the ions are essentially free), one would expect an absolute saturation magnetic moment of 10 Bohr magnetons. These data indicate that the absolute saturation moment of dysprosium is probably not this large. This may be interpreted as meaning that the 4f electrons are not completely free from the influence of neighboring atoms.

On the other hand, it has been necessary to assume in the case of iron, nickel, and cobalt, that the orbital angular momentum was almost completely quenched, in order to explain the magnitude of their absolute saturation magnetization. If the orbital moment were completely quenched in dysprosium, one would expect a saturation moment of 5 Bohr magnetons. The absolute saturation moment is obviously much larger than this, as measured values of the magnetic moment larger than 5 Bohr magnetons have been found in regions where the element is far from saturation. This is the first pure metal, to the author's knowledge, in which orbital angular momentum has been shown to play a definite part in ferromagnetic properties.

Quenching of the orbital angular momentum is, of course, due to the proximity of neighboring atoms in the crystal lattice. Since it appears

that the quenching is far from complete in dysprosium, one is forced to assume that the atoms are nearly free, at least as far as the 4f electrons are concerned. The effect of this conclusion on the magnitude of the Heisenberg exchange integral is not obvious.

The unusual shape of the magnetization vs 1/H curves must be explained. Perhaps a possible explanation can be made in terms of a system of two magnetic phases. The general shape of the curves could be explained by such a system.

A crystal structure change could be a possible mechanism for a system of two magnetic phases. Because of the X-ray investigation of dysprosium over the ferromagnetic range (26), this mechanism seems unlikely.

An impurity such as iron surrounded by dysprosium might be another mechanism for the system. The spectrographic analysis for iron showed less than 2000 ppm, but, as no quantitative standards for iron were yet available, this was given as a maximum limit for the iron impurity.

The iron cerium intermetallic compound has been found to have a serious effect on the magnetic properties of cerium metal. Several of these compounds are known to be ferromagnetic and in particular compounds with as low as 100 ppm concentration of iron are believed to be ferromagnetic, having a Curie point somewhere between 76°-300°K (33).

Whether the iron impurities are serious in dysprosium and erbium, and whether iron is the cause of the apparent system of two magnetic phases, will be answered only after better quantitative methods of analysis have been developed and controlled experiments performed.

One further mechanism for a system of two magnetic phases is the possibility that dysprosium is ferromagnetic in one temperature range and

antiferromagnetic in another.

Before attempting to explain the magnetic phenomena of dysprosium and erbium on the basis of such a system it would perhaps be wise to recall several important facts about magnetic systems. First, if the system is in its lowest energy state when the spins of neighboring atoms are parallel, the substance is ferromagnetic. If the system is in its lowest energy state when the spins are antiparallel, the substance is antiferromagnetic. Which of these energy states is lowest depends on the coupling constants involved with nearest neighbor and next nearest neighbor atoms. Thus, there is no a priori reason why a ferromagnetic system can not be changed into an antiferromagnetic system just by changing the distance between neighboring atoms. Also there is no a priori reason why the difference in energy between the antiferromagnetic system and ferromagnetic system can not be small. Second, it is an experimental fact[1] that some lattice parameters of some ferromagnetic substances increase as the temperature is decreased through the Curie point. This increase continues with decreasing temperature until the substance reaches nearly its full saturation magnetization. At this point the coefficient of thermal contraction once more becomes dominant, and as the temperature is further decreased, the lattice parameters once more decrease. Similar changes in some of the lattice parameters near the Curie temperature have also been observed for antiferromagnetic substances (34, 35).

Banister (26) has suggested a possible explanation of the increase of the lattice parameters (i.e., the c_o axis for the rare earths) near

[1]See Banister's work on gadolinium (26) or the discussion in Bozorth (31), pp. 447-448.

the Curie point. He notes that the interaction between the "molecular field" (assumed to be in the c_0 direction) and 5d electrons would tend to increase the probability of the 5d electrons being in a plane perpendicular to the c_0 axis. The strength of the bond between neighboring atoms in the c_0 direction would then be decreased as the density of the electrons (which essentially determines the strength of the bond) between these two atoms would be decreased. Since the strength of the interaction depends upon the magnitude of the "molecular field", which in turn depends upon the magnitude of the magnetization, the effectiveness of the bond will continue to decrease until the "molecular field" becomes nearly constant, or in other words, until the substance has reached its saturation magnetization. When the substance has reached its saturation magnetization the coefficient of thermal contraction once more becomes dominant and the parameter begins to decrease once more.

With the above facts in mind, it is now possible to suggest another mechanism for a system of two magnetic phases to explain the magnetic behavior of dysprosium.

As can be seen from Banister's X-ray data on dysprosium (Figure 18), the c_0 axis tends to decrease as the temperature is lowered from room temperature until a minimum is reached in the neighborhood of 175°K. It is now supposed that dysprosium is in an antiferromagnetic state, as indicated by the form of the magnetic anomaly, and by the fact that the susceptibility is field dependent only for high fields. The antiferromagnetic arrangement of atoms may be like that suggested by Yin-Yuang Li (36). As the temperature is further decreased the c_0 axis tends to

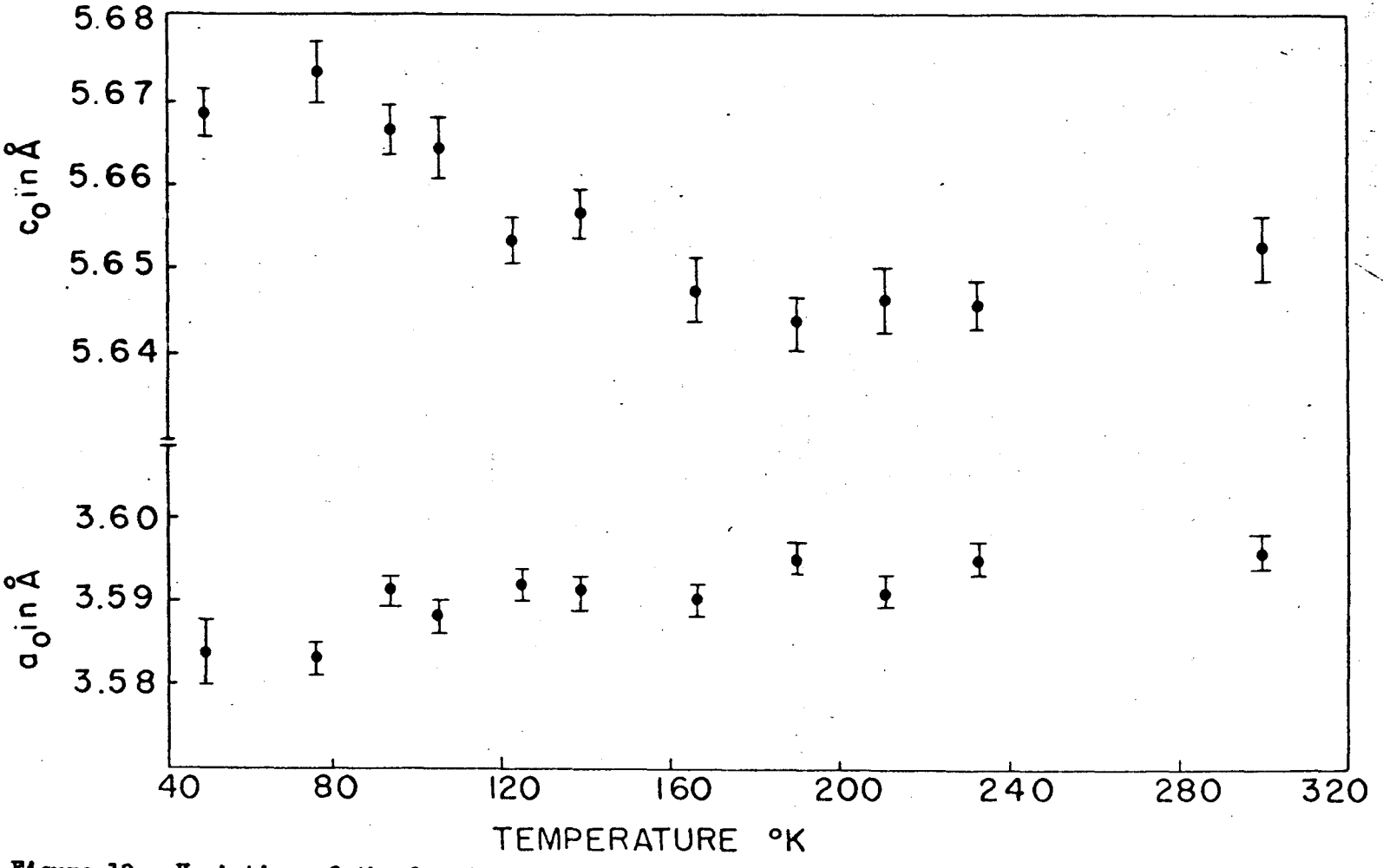


Figure 18. Variation of the lattice parameters of dysprosium with temperature (after Banister).

increase, which is in the direction such as to favor ferromagnetism. If now the energy separation between the antiferromagnetic state and ferromagnetic state is small, then one would expect that the critical separation distance between atoms would soon be reached by the expanding c_o axis. At about 92°K this critical distance presumably has been reached, the exchange integral changes sign, and the lowest energy state of the system is such that the ferromagnetic state is favored. As the temperature is lowered further the ratio of R/r becomes more and more favorable to the ferromagnetic state as the c_o axis continues to increase. Below the ferromagnetic Curie point at 92°K the magnetic isotherms (Figure 7) begin to fall closer and closer together indicating that dysprosium is nearly saturated temperature-wise. In this temperature region the coefficient of thermal contraction once more becomes dominant as expected, and again the c_o axis begins to decrease in the direction favorable to the antiferromagnetic state. From Banister's data one would expect that the critical distance, which determines the sign of the exchange integral, would be reached in the neighborhood of 40°K. Actually the magnetic data shows that the critical distance is reached around 20°K. Thus, the apparent anomaly at the hydrogen point observed in dysprosium is an indication that dysprosium is nearly antiferromagnetic again.

The fact that the magnetic moment vs 1/H isotherms in the 31°-80°K temperature range appear to consist of two intersecting straight lines means that for some reason some of the antiferromagnetic sublattices do not change completely over to ferromagnetic sublattices, and it is only at high applied fields that the susceptibility of this antiferromagnetic sublattice becomes field dependent and is observable.

Neutron diffraction studies of dysprosium in the temperature range of 90°K to 175°K and possibly at 4°K will confirm or disprove this hypothesis.

An alternative explanation for the strange behavior of the σ vs 1/H curves might arise from the fact that the neighboring crystal fields of the surrounding dysprosium atoms might cause a splitting of the lowest atomic level of the dysprosium ion. In such a case, there would be a temperature dependency of the population of these levels, and further the "g" values, spacings, and magnetic moments of these levels might be profoundly influenced by the applied magnetic fields used in these experiments.

The explanation of the magnitude of the absolute saturation magnetisation must of course await a satisfactory interpretation of the σ vs 1/H curves, as well as more accurate extrapolated values of the saturation moments. Until this is forthcoming, it is perhaps not profitable to speculate.

C. Erbium

Although the magnetic data for erbium are in many respects similar to those of dysprosium, it would be informative to point out the several experimental facts that differ between the two elements. The first difference is in the nature of the break near the Curie point of the resistivity vs temperature curves of the two elements (20). In erbium the break is rather sharp as a function of temperature very similar to the corresponding discontinuity in the slope for gadolinium. Dysprosium, on

the other hand, appears to have two discontinuities in the slope. The first is in the neighborhood of 190°K, and the second at about 160°K. Between the two discontinuities the resistance is nearly constant, or possibly increases slightly with decreasing temperature.

The second difference between the two elements is found in the study of their Hall coefficients (37) in the temperature region where the susceptibility of these elements becomes field dependent. Dysprosium exhibits a rapidly increasing negative Hall coefficient as the temperature is lowered towards 200°K. This is quite characteristic of a ferromagnetic substance as it approaches its Curie point (38). At about 180°K the Hall coefficient reaches a maximum. As the temperature is further lowered the Hall coefficient decreases rapidly and changes sign at about 120°K. The Hall coefficient of erbium remains negative down to 20.4°K, and shows no indication of anomalous behavior.

The third difference in the two elements is, of course, the apparent absence of a well defined magnetic anomaly in erbium that is associated with state A_1 of dysprosium.

All of these experimental observations are dependent to a greater or lesser extent upon the magnetic properties of the two elements, and suggest that while the magnetic properties of both erbium and dysprosium may be explained qualitatively in the same way, it will be necessary to further modify the explanation in the case of one of the elements to explain the difference of the Hall effect and resistivity measurements.

Recently the preliminary neutron diffraction study of metallic erbium has been completed at Oak Ridge (39). These data in the temperature range.

of 90°K to about 25°K are rather confusing and are not completely understood. These data indicate that some magnetic ordering sets in at about 78°K with the magnetic moment perpendicular to the c_0 axis. At about 68°K additional complicating features appear in the form of extra reflections. Below this temperature down to 46°K the ordering seems to become more pronounced and the extra reflections become more intense. From 20.4°K to 4°K there is a high degree of ordering parallel to the c_0 axis which would appear to be of a ferromagnetic nature, and the intensities of the extra reflections are diminished.

The possibility of understanding the Oak Ridge data in terms of an antiferromagnetic ordering in certain temperature ranges has proved to be unfruitful using the type of antiferromagnetic sublattice suggested by Yin-Yuang Li (36). This does not mean, however, that the possibility of understanding the magnetic properties of dysprosium in terms of antiferromagnetism is precluded. It may well be that antiferromagnetism is not quite developed in erbium as indicated by the absence of any magnetic anomaly, and the differences between the Hall effect and resistivity measurements of the two elements. As noted above, this hypothesis will stand or fall only when neutron diffraction data are obtained for dysprosium.

It should be pointed out that the high magnetic moment of erbium, as in the case of dysprosium, is significant. Magnetic moments have been measured for erbium that are much higher than the 3 Bohr magnetons predicted for the absolute saturation moment from the spectrographic state $^4I_{15/2}$ if only the spins of the unpaired 4f electrons were contributing to the ferromagnetism.

D. Discussion of Errors

As mentioned in the introduction, the primary purpose of this investigation was to determine, if possible, the absolute saturation magnetization of gadolinium, dysprosium, and erbium. Thus, the only numbers cited in this study for which particular attention has been paid in regard to the estimation of their accuracy, are those which have been cited as values of the absolute saturation magnetization for the various elements.

In order to obtain an experimental value of the absolute saturation moment, it will be recalled that the following procedure was used. 1) At a given temperature a number of magnetic moments were measured at various fields. 2) It was found that when the magnetic moments, measured in step one, were plotted as a function of 1/H, they appeared to lie on a straight line. 3) Assuming then that the "true" physical law which governs the variation of magnetic moment with applied field is a linear function of 1/H, the least squares process was applied to the experimental data, and the intercept on the magnetic moment axis determined. This intercept is then the saturation moment at the given temperature. 4) Steps one through three are then repeated for a number of various temperatures. 5) It was found when the saturation moments, obtained in step four, were plotted against $T^{\frac{3}{2}}$, they appeared to lie on a straight line. 6) Assuming then that the "true" physical law which governs the variation of saturation magnetic moment with temperature is a linear function of $T^{\frac{3}{2}}$, the least squares process was applied to the experimental data, and the intercept on the saturation moment axis determined. This intercept is then the

absolute saturation moment.

The validity of this experimental value of the absolute saturation moment rests entirely on the validity of the assumptions made in steps three and five. This experimental procedure seems to give an answer which is justifiable theoretically, at least in the case of iron, cobalt, nickel, and gadolinium.

The only alternative to making these or similar assumptions is to make a direct measurement of the absolute saturation magnetic moment at 0°K and using an infinitely high applied field, which is of course impossible.

Both systematic errors and random errors were present in this study. The random errors are believed to be responsible for the deviation of the experimental points from the straight lines in Figures 3, 11, 12 and 13; and such deviations were assumed to be random in estimating the error in the value of the saturation magnetization.

The author is aware of only one systematic error in the experimental procedure. This error was present because it was not possible to place the unknown sample in the exact position occupied by the standard sample which was used in the calibration process. The existence of this systematic error became apparent when it was not possible to repeat the calibration exactly when the standard sample was removed and then replaced again. This error had the effect of moving the lines drawn through the experimental points up or down, but parallel to themselves. The calibration was carried out about ten times to obtain some idea of the error that could be expected from this source. The standard deviation for this type of error was about 0.8 per cent. As can be seen from the remainder of

this discussion, this systematic error sets the limits of the accuracy for the experimental study.

To obtain an estimate of the error of each individual measurement, the usual standard deviation process was employed on equation 4). Equations 6) and 7) were also studied so that the effect of errors in temperature and applied field measurements could be estimated. Listed below are typical values of the various quantities measured in this study. The values of a, and b (equations 6) and 7) are those of gadolinium and are assumed to be correct to as many figures as desired. The errors shown after the typical values are the estimated standard deviations for these quantities. The symbols have the same meaning as employed throughout this study; and in addition,

$F/g = \Delta M$ = apparent change in mass of the unknown when placed in the non-uniform magnetic field,

$F'/g = \Delta M'$ = apparent change in mass of the standard sample of iron when placed in the non-uniform magnetic field,

m' = mass of standard sample of iron

and, σ' = the saturation magnetic moment of iron at 20°C.

$\Delta M = \Delta M' = 7.00 \pm 0.01$ gms.

$m = m' = .0600 \pm 0.0001$ gms.

$\sigma' = 217.8 \pm 0.05$ cgs units

$T = 20 \pm 1°K$

$H = 5000 \pm 50$ oersteds

$b = 1 \times 10^{-4}(°K)^{-3/2}$

$a = 170$ oersteds^{-1} .

The magnetic moment was considered to be a function of the following variables:

$$\sigma(\Delta M, \Delta M', m, m', \sigma', T, E) .$$

The standard deviation was thus calculated using the following expression:

$$S.D. = \left[\left(\frac{\partial\sigma}{\partial\Delta M}\right)^2 (d\Delta M)^2 + \left(\frac{\partial\sigma}{\partial\Delta M'}\right)^2 (d\Delta M')^2 + \cdots\cdots\right]^{\frac{1}{2}}$$

Using the typical values and their standard deviations, the standard deviation for each individual measurement of the magnetic moment was found to be about 1.4 cgs units.

The second step of the experimental procedure was to employ the method of least squares to the individual measurements. In this process the deviations of the individual measurements from the straight line were considered random. The least squares process indicated that the standard deviation in the extrapolation to find the saturation moment at a given temperature was of the order of 1.5 cgs units.

The third step was again to employ the method of least squares to the values of the saturation moments obtained in the second step. The deviation of the individual values of the saturation moments from the straight line were again considered random. The least squares process indicated that the standard deviation was of the order of .9 cgs units. That is, if it were possible to measure the absolute saturation moment a number of times, 74 per cent of the measurements would fall within .9 cgs units of the cited value for the absolute saturation moment for gadolinium.

As pointed out above, the systematic error was probably greater than this; and therefore, is the limiting factor of the accuracy for this study.

As noted in the section on the results of dysprosium, no attempt was made to use the least squares process in the extrapolations of these data.

Because the high field data were rather limited, it was felt that such a procedure was not warranted. The standard deviation cited for the absolute saturation moment was a guess, based on attempts to fit various straight lines through the data points, and upon past experience. As noted above, the value of 273 cgs units cited for the absolute saturation magnetic moment of dysprosium is probably a minimum value. The importance to be attached to the other value of 299 cgs units must of course await measurements at higher fields, and a satisfactory interpretation of the magnetization curves.

To summarize, the individual measurements of the magnetic moment of gadolinium, dysprosium and erbium are probably accurate to about 1.3 per cent (i.e., 0.8 per cent systematic error, .5 per cent random error); the individual saturation magnetic moments in the case of gadolinium are probably accurate to about 1.2 per cent; for dysprosium, the saturation magnetic moments are probably accurate to about 2.5 per cent; the value for the absolute saturation moment for gadolinium is probably accurate to at least 1.0 per cent. The absolute saturation magnetic moments of dysprosium are probably accurate to about 1.3 per cent using low field extrapolations, and to about 2.5 per cent using the high field extrapolations provided the cited values have any physical meaning.

B. General

A break in the temperature-resistivity curve has been shown to be a reliable guide in the predicting of the ferromagnetism of erbium, and indicates that the break in the neighborhood of 12°K for cerium (40) should be investigated for possible ferromagnetism.

The extreme "hardness" of dysprosium and erbium shows that future attempts to measure their absolute saturation moments more accurately must lie with the availability of high magnetic fields (i.e., of the order of 50K oersteds or greater) and/or single crystals.

The low Curie point of erbium further points out that one must be prepared to do extensive work in the helium-hydrogen temperature range, and possibly even into the magnetic cooling range.

In conclusion, this study of gadolinium, dysprosium, and erbium surely suggests that the rare earth metals will be as fruitful a field for the study of ferromagnetic phenomena as the rare earth salts have been for paramagnetic phenomena in the past.

V. SUMMARY

1. The magnetic moment of gadolinium was measured in applied fields of 4,000-18,000 oersteds, and over the temperature range of 20.4°K to 320°K.
2. The ferromagnetic absolute saturation moment of gadolinium was found to be 253.6 ± 0.9 cgs units, confirming the work of Trombe (18, 19). This absolute saturation moment corresponds to about 7.12 Bohr magnetons.
3. The Curie point for gadolinium was determined by two different methods. The two determinations do not agree.
4. The magnetic moment of dysprosium was measured in applied fields of 4,000-18,000 oersteds, and over the temperature range of 20.4°K to 205°K.
5. The susceptibility of dysprosium was shown to be field dependent in the approximate temperature range of 90°K to 172°K. Below about 90°K dysprosium appeared to be truly ferromagnetic, confirming the observation of Trombe (21, 22).
6. The magnitude of the measured values of the magnetic moment of dysprosium indicates that the orbital angular momentum must contribute to the ferromagnetism.
7. An absolute saturation magnetic moment of at least 8 Bohr magnetons was indicated by the data obtained in the temperature range of 31.25°K to 80°K.

8. The strange behavior of the magnetization vs 1/H curves of dysprosium was noted, and possible explanations were set forth.
9. The magnetic moment of erbium was measured for applied fields of 4,000-18,000 oersteds, and over the temperature range of 20.4°K to 71°K.
10. The susceptibility of erbium was shown to be field dependent below about 55°K.
11. Erbium appeared to be truly ferromagnetic at 20.4°K.
12. The magnitude of the measured values of the magnetic moment of erbium indicates that the orbital angular momentum must contribute to the ferromagnetism.
13. The similarities and differences of the magnetic behaviors of erbium and dysprosium were noted.

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VII. ACKNOWLEDGMENTS

The author wishes to acknowledge his indebtedness to Dr. F. H. Spedding for the opportunity of performing this investigation, and for his generous help and interest; to Dr. E. Legvold for his numerous suggestions, his willingness to spend many hours assisting in taking data and discussing the investigation, and above all for the deep interest he has shown in the author's scholastic and personal life; to Dr. Jack Powell for preparing the rare earth salts; and to Dr. A. H. Daane, Mr. Richard Barton, and Mr. David Dennison for preparing the metal samples.

Special thanks are due for Mr. Robert Anderson and Mr. William Sylvester for their help in constructing the numerous pieces of equipment.

The author also wishes to express publicly his gratitude to his wife, who made the past six years of study possible with her encouragement and patience.

VIII. APPENDICES

Included in these appendices are the measured values of the magnetic moment, the calculated values of the magnetizing field, and the extrapolated values of the saturation magnetic moment for gadolinium, dysprosium, and erbium. The numerous calibration curves for the gradient of the magnetic field and for the applied field are not recorded here. Such calibration curves, together with the original calculations, are on file at the Low Temperature Laboratory, Institute for Atomic Research, Iowa State College, Ames, Iowa.

The symbols used in these appendices have the same meaning and units as those used throughout the text.

A. Gadolinium

1. Measured values of the magnetic moment of gadolinium

H	$\sigma_{H,T}$
T=20.4°K	
6,850	240.4
10,050	242.7
11,950	243.6
14,150	245.3
15,950	245.5
17,750	247.3
T=26.0°K	
5,600	244.6
6,200	245.6
7,450	246.9
8,250	245.9
9,750	247.3
12,600	247.6
15,550	249.9
17,900	248.3
T=39.6°K	
5,600	239.8
6,300	241.2
7,200	242.5
8,200	242.3
9,550	242.9
12,500	244.3
14,950	244.7
17,800	244.3
T=49.5°K	
5,550	240.1
6,150	240.0
7,550	241.3
8,600	241.8
10,150	242.6
12,350	242.2
14,900	244.5
17,850	242.7

H	$\sigma_{H,T}$
T=57.8°K	
5,000	235.1
6,650	236.6
7,450	238.2
8,450	239.2
10,050	239.4
12,500	239.2
14,300	241.4
17,650	239.7
T=75.2°K	
5,450	229.7
6,100	230.0
7,250	232.8
8,300	233.0
9,900	233.3
13,650	235.0
15,050	236.8
17,350	235.3
T=85.9°K	
5,450	226.3
6,600	227.4
7,150	228.3
8,650	230.1
10,050	229.9
12,800	231.2
15,300	232.4
17,850	231.2
T=89.9°K	
5,450	226.5
6,500	227.1
7,150	228.3
8,100	229.1
9,950	228.7
12,300	229.3
14,650	230.8
17,900	229.2

H	$\sigma_{H,T}$
T=113.8°K	
5,700	219.4
6,750	216.8
7,400	219.0
8,250	220.5
9,850	220.4
12,450	221.5
15,050	222.2
17,850	221.4
T=133.4°K	
5,550	209.0
6,500	210.6
7,400	211.2
8,450	212.3
10,150	211.6
12,800	213.2
15,300	214.9
17,900	213.8
T=150.8°K	
5,450	203.4
6,050	205.9
7,150	204.5
8,400	205.8
10,050	204.8
12,400	205.6
15,150	206.9
17,850	206.4
T=168.6°K	
5,500	195.8
6,150	197.1
7,350	197.6
8,200	197.3
10,300	197.2
17,700	197.1
15,150	198.3
17,950	197.5

H	$\sigma_{H,T}$
T=187.4°K	
5,500	184.9
5,950	184.5
7,250	186.7
8,250	187.0
9,950	186.6
12,850	187.9
15,250	188.9
17,900	188.2
T=207.3°K	
5,500	174.3
6,100	174.2
7,500	175.4
8,250	175.3
10,300	176.8
13,000	176.7
15,250	178.2
17,850	177.6
T=231.4°K	
5,500	157.3
6,350	158.1
7,450	158.8
8,200	159.4
10,200	160.1
12,400	162.0
15,550	162.4
17,850	162.2
T=253.7°K	
5,600	138.9
6,300	139.1
7,500	139.8
8,300	139.6
9,900	141.4
12,350	142.6
15,200	145.2
17,900	143.3

2. Saturation magnetic moment of gadolinium at T°K

T°K	σ_{∞}, T
20.4	250.3
26.0	250.8
39.6	246.9
49.5	245.2
57.8	242.9
75.2	239.0
85.9	234.7
89.9	231.4
113.2	223.9
133.4	216.8
150.6	207.4
168.6	198.5
187.4	190.3
207.3	180.3
231.4	164.9
252.7	146.6

3. Dysprosium

1. Measured values of the magnetic moment of dysprosium

H	$\sigma_{H,T}$
T=20.4°K	
2,950	154.0
4,800	177.5
5,600	185.1
6,200	190.3
7,150	198.0
8,350	203.5
9,800	209.5
11,100	215.1
12,400	218.5
13,550	219.8
15,200	226.4
16,150	229.1
17,100	231.8
17,850	233.4
T=31.25°K	
5,450	198.9
5,950	200.1
7,200	209.6
8,650	219.2
9,800	224.9
11,050	231.5
12,300	234.9
14,050	239.1
15,400	243.7
16,150	244.4
16,850	246.2
17,850	249.1
T=36.0°K	
2,850	159.7
4,650	191.4
5,350	197.6
6,350	204.5
7,250	210.5
9,050	220.9
9,950	224.7
10,800	228.3
12,400	233.6
16,150	245.9
17,150	248.0
17,950	247.9

H	$\sigma_{H,T}$
T=50.0°K	
2,850	162.1
4,650	187.3
6,700	206.7
7,250	210.6
8,800	219.9
9,750	223.4
11,150	231.6
13,800	235.0
15,600	237.8
15,050	240.4
16,150	242.4
17,050	244.8
17,900	246.7
T=65.0°K	
2,750	163.0
4,800	193.3
5,700	199.2
6,300	201.2
7,200	199.3
9,550	223.4
11,000	227.4
12,300	231.4
13,850	234.6
15,100	236.9
16,150	239.3
16,950	241.9
17,850	243.7
T=80.0°K	
2,850	160.4
4,700	186.7
5,400	193.9
6,100	198.3
7,250	205.7
8,350	213.1
9,850	219.0
11,050	225.5
12,350	228.9
13,750	231.9
15,250	233.6
16,050	235.5
16,900	236.7
17,950	239.1

H	$\sigma_{H,T}$
T=91.4°K	
3,050	140.1
4,950	173.4
5,500	180.1
6,350	199.5
7,250	194.8
8,600	202.2
10,050	209.3
11,100	213.2
12,300	218.0
13,450	219.8
16,000	226.8
17,950	229.2
T=103.0°K	
3,050	60.3
5,000	147.9
5,500	157.2
6,300	171.4
7,350	188.5
9,050	196.4
9,850	202.9
11,050	205.9
12,400	210.4
13,480	212.3
16,050	219.3
18,050	222.5
T=113°K	
2,950	13.6
4,800	79.4
5,800	124.0
6,400	137.1
7,500	162.7
9,450	185.5
10,400	190.8
11,700	196.5
12,650	199.7
14,050	205.3
16,150	210.1
17,850	211.3

H	$\sigma_{H,T}$
T=121.0°K	
3,150	11.7
5,000	24.0
5,700	42.4
6,450	79.6
7,200	109.7
8,900	147.0
10,000	165.6
11,000	173.9
12,500	183.0
13,850	189.5
15,800	194.4
17,950	199.3
T=135.0°K	
3,100	8.7
5,650	17.7
6,350	21.1
7,200	33.2
9,000	95.7
9,950	120.2
11,150	130.4
12,600	155.8
13,700	161.7
15,900	173.4
17,850	180.9
T=137.7°K	
3,050	8.0
5,000	14.2
5,550	16.3
6,300	19.0
7,300	28.4
8,850	72.4
10,050	110.7
11,100	128.9
12,400	145.0
13,900	156.5
15,900	168.4
17,900	176.4

H	$\sigma_{H,T}$
T=145.5°K	
3,000	10.0
4,900	14.0
5,650	15.4
6,150	17.3
7,350	21.8
8,550	32.5
9,800	66.5
11,250	103.5
12,600	122.5
13,950	135.8
16,000	150.9
18,000	161.3
T=153.4°K	
3,100	7.7
4,850	11.6
5,600	13.6
6,350	16.3
7,300	19.3
8,400	24.3
10,200	44.3
11,450	75.1
12,600	97.1
14,000	113.5
15,900	129.9
17,900	143.1
T=161.0°K	
3,100	9.1
5,050	13.5
5,650	14.7
6,600	17.6
7,300	19.5
8,400	23.6
10,000	31.4
11,000	44.4
12,550	73.4
13,350	90.7
15,900	108.0
18,050	122.3

H	$\sigma_{H,T}$
T=168.4K	
3,100	10.9
5,000	14.3
5,850	16.2
7,200	20.8
8,600	36.1
9,900	33.2
11,200	45.9
12,550	64.1
13,700	73.0
15,900	87.6
18,000	98.2
T=173.0°K	
3,100	10.8
5,150	17.5
6,100	19.8
7,300	24.0
8,500	30.0
10,300	44.3
11,200	51.9
12,550	59.4
13,700	62.7
16,000	76.1
18,000	86.0
T=175.5°K	
3,100	11.3
5,450	19.9
6,300	28.3
7,350	28.9
8,450	39.4
10,400	44.9
12,300	52.2
14,150	59.8
15,950	67.0
17,950	74.4

H	$\sigma_{H,T}$
T=180.7°K	
3,000	11.0
4,900	17.5
6,500	21.9
7,200	24.7
8,450	28.5
10,250	35.3
12,200	41.6
14,050	47.2
16,000	53.9
17,900	60.9
T=185.8°K	
2,900	7.7
5,150	14.4
6,800	18.1
7,950	22.1
9,700	27.5
10,750	30.9
12,250	35.1
13,650	38.2
16,150	45.6
18,050	50.9

H	$\sigma_{H,T}$
T=195.8°K	
3,150	4.9
5,000	10.5
5,550	11.9
6,500	14.0
7,450	16.3
9,150	19.5
10,550	23.2
12,300	26.6
14,200	30.2
16,250	34.6
18,050	38.3
T=203.2°K	
3,000	5.6
5,000	10.0
5,700	10.7
6,400	12.2
7,300	13.9
8,400	15.9
10,000	19.0
11,850	25.5
13,550	27.7
16,050	29.5
18,100	33.7

2. Saturation magnetic moment of dysprosium at T°K

"$\sigma_{\infty,T}$ low" is the saturation magnetization determined from low applied field data (i.e., less than about 12,000 oersteds).

"$\sigma_{\infty,T}$ high" is the saturation magnetization determined from high applied field data (i.e., greater than about 12,000 oersteds).

T°K	$\sigma_{\infty,T}$ high	$\sigma_{\infty,T}$ low
31.25	290.0	271.2
35.0	286.7	267.2
50.0	282.5	267.3
65.0	275.2	261.3
80.0	261.6	261.6

C. Erbium

1. Measured values of the magnetic moment of erbium

H	$\sigma_{H,T}$
T=20.4°K	
3,150	67.8
4,600	87.8
6,060	103.8
7,150	114.3
8,950	130.0
9,950	137.5
11,250	146.5
12,350	154.9
14,050	165.5
15,350	175.9
16,150	181.1
17,050	187.7
17,900	193.5
T=35.0°K	
3,150	9.6
5,000	14.6
5,650	17.1
6,150	20.3
7,300	33.8
8,500	56.8
9,850	86.6
11,200	107.2
12,600	124.3
13,800	140.0
16,000	162.9
17,900	177.5
T=40.5°K	
3,050	9.1
5,000	14.3
5,750	16.0
6,300	17.6
7,600	21.8
8,800	27.2
9,800	36.7
11,150	57.0
12,700	83.0
14,000	98.1
16,200	122.4
18,000	138.9

H	$\sigma_{H,T}$
T=45.8°K	
3,200	8.7
5,100	13.8
5,900	15.7
6,500	17.0
7,300	19.1
8,750	22.6
10,000	26.1
11,250	30.2
12,800	36.3
13,650	51.5
16,000	90.3
18,000	118.6
T=51.0°K	
3,250	7.7
4,900	11.4
5,500	12.7
6,100	14.2
7,550	17.8
9,750	23.3
11,650	27.9
13,600	32.7
16,200	47.9
18,050	69.6
T=61.2°K	
3,250	8.5
4,850	10.4
5,600	11.7
6,250	13.1
7,550	16.1
9,050	18.9
10,600	22.5
11,600	24.8
13,350	28.5
16,300	35.2
18,050	40.5

H T=71.0°K	$\sigma_{H,P}$
3,100	5.5
4,800	10.2
5,500	11.3
6,400	13.3
7,400	15.3
9,100	19.0
10,600	22.3
11,850	24.9
13,500	28.5
16,000	36.0
18,000	41.6